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SIMPLE INSTRUMENT FOR TITRIMETRY WITHOUT VISUAL INDICATORS. GASOMETRIC TITRATIONS

XII. ARGENTOMETRY

by

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The present communication has two purposes. The first is to show that the gasometric titration method can be used not only for acid-base and redox reactions (as already reported in previous papers[1]), but also for precipitation and complex-formation reactions. The second is to describe an improved model of the titration apparatus (Fig. 1).

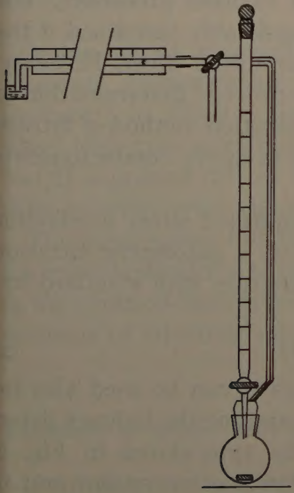

Fig. 1. Improved model of titration apparatus.

DESCRIPTION OF INSTRUMENT

The titration vessel is a 50 ml flask, provided with a hollow glass stopper, through which passes the tip of a 10 ml buret and a capillary tube, which connects the flask and the top of the buret. The upper end of the buret is closed with a glass stopper. A three-way stopcock establishes connection between the top of the buret and horizontal glass tubing of suitable length and internal diameter (5, 2 and 1 mm for titrations of solutions respectively 0.1, 0.01 and 0.001N), the free extremity of which is bend downward and dips into water. A scale graduated in mm or 0.5 mm can be adjusted to any point of this tube. If solutions up to 0.05N are being titrated, the titration vessel should be protected from temperature changes by shielding it with asbestos paper. A magnetic stirrer provides the indispensable stirring of the sample solution.

GENERAL PROCEDURE

Transfer a measured volume of the sample solution to the titration flask and add other reagents and indicator if required. Connect the flask with the buret. Fill the horizontal glass tube with water, applying suction through the free extremity of the three-way stopcock. Turn the plug of this stopcock so as to establish connection only between the buret and the glass tube. Put the magnetic stirrer in motion.

Apply the O division of the scale to the extremity of the water column. Add measured increments of titrant (for instance 1 ml) to the sample solution, wait until the extremity of the water column in the tube remains steady, and then read in mm the length of the displaced water column. Plot the volume of titrant added against the length of the displaced water column. Extend the straight-line portions of the curve to intersect. The intersection marks the end-point.

It happens sometimes, chiefly during titration of dilute solutions, that the extremity of the water column in the tube does not remain sufficiently steady to allow an unequivocal reading. In such a case it is better to make the addition of the titrant and the reading of the water level in the tube at fixed intervals of time (1 or 2 minutes for example). If the concentration of the solutions is 0.01N or less, titrating and titrated solutions must be at the same temperature.

Titration of silver with hydrazine sulfate

Brown and Boyd[2] published recently a paper on an argentometric procedure for borohydride determination. The analysis is based on the reaction:

$$8\ Ag^+ + BH_4^- + 8\ OH^- \xrightarrow[\text{diamine}]{\text{ethylene}} 8\ Ag^\circ + H_2BO_3^- + 5\ H_2O \qquad (1)$$

The precipitated silver is removed by filtration and the excess silver ion in the solution is determined after acidification by the standard Volhard procedure. The authors state that "the analytical procedure could be considerably simplified if the excess silver ion could be titrated in presence of the precipitated silver. However, the black colour of the precipitated silver makes a colorimetric determination of the end-point impractical. Thus an attempt to apply the titration method of Bloom and McNabb[3] failed for this reason. No attempt was made to apply conductometric or potentiometric methods to such a titration".

The problem of titrating silver ion in presence of precipitated silver in alkaline medium, as posed by Brown and Boyd, can be solved by a gasometric titration procedure. The analysis involves direct titration of the mixture with standard hydrazine sulfate solution according to the equation:

$$4\ Ag^+ + N_2H_4 + 4\ OH^- \rightarrow 4\ Ag^\circ + N_2 + 4\ H_2O \qquad (2)$$

in the simple instrument described above. The same method can be used also for the direct titration of silver in an insoluble halide residue and for the indirect determination of cyanide or iodide ions. The graphs are of the type shown in Fig. 2. The intersection of the lines corresponding to the reaction (gas evolution) and to excess titrant (no gas evolution) signals the end-point.

Reagents

Hydrazine sulfate, 0.05, 0.025 and 0.0025M solutions.
Sodium hydroxide, 0.5 and 5N solutions.
Ammonium hydroxide, concentrated solution.

Procedure 1

Transfer 5.00 to 10.00 ml of the neutral sample solution which contains silver ions to the titration flask (or suspend a known amount of the insoluble silver salt in 5 ml of water), add sodium

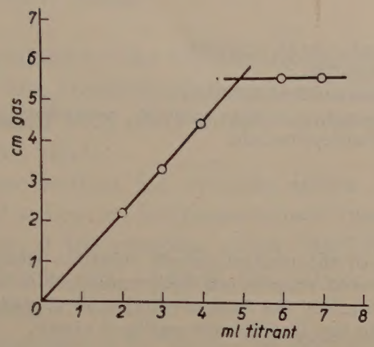

Fig. 2. Gasometric titration of 5.00 ml 0.0100M $AgNO_3$ solution with 0.0025M $N_2H_4.H_2SO_4$ solution (internal diameter of gas measuring tube 3 mm). End-point 4.98 ml (theoretical 5.00 ml).

hydroxide and concentrated ammonium hydroxide solutions (see Table I for quantities of reagents), connect the flask with the buret which contains the hydrazine sulfate solution and titrate following the instructions outlined above.

Interferences

Noble metals, copper(II) and mercury(II) ions, as well as oxidizing anions, such as iodate, permanganate and hypochlorite must be absent, since they also oxidize hydrazine in alkaline medium. Cyanide and iodide subtract their equivalent of silver ions from reduction, if the sodium hydroxide alkalinity is small. If sufficient NaOH is present neither those nor other anions which form even more soluble silver salts interfere with the analysis.

The ammonium hydroxide excess over the quantity necessary to dissolve the silver oxide should be as small as possible. A great excess of free ammonium hydroxide in the titration flask gives rise to contractions of the volume of the system when fresh volumes of titrating solution are introduced.

Titration of iodide with silver nitrate

According to the gasometric titration procedure outlined below iodide ions can be titrated directly with silver nitrate solution in alkaline medium. Hydrazine functions as gasometric indicator, reacting with excess silver ion after all the iodide has been transformed into silver iodide. The method is based on the fact that the very slightly soluble silver iodide does not react with hydrazine in moderately strong alkaline medium, whereas the cation of more soluble silver salts reacts according to equation 2.

The graphs are of the type shown in Fig. 3. The intersection of the line (abscissa) corresponding to the main reaction (no gas evolution) and the line corresponding to the reaction of the titrant with the indicator (gas evolution) marks the end-point.

Reagents

Silver nitrate, 0.2, 0.05 and 0.01M solutions.

Sodium hydroxide, 0.5N solution.

Ammonium hydroxide, concentrated solution.

Indicator: concentrated hydrazine sulfate solution, neutralized with 0.5N sodium hydroxide solution to the rose tint of phenolphthalein.

Procedure 2

Transfer 5.00 to 10.00 ml of the neutral sample solution, which contains iodide ion, to the titration flask, add concentrated ammonium hydroxide and indicator solutions (see Table II for quantities of reagents), connect the flask with the buret which contains the silver nitrate solution and titrate, following the instructions outlined above.

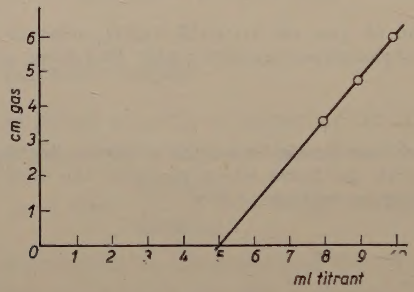

Fig. 3. Gasometric titration of 5.00 ml 0.01M KI solution with 0.01M $AgNO_3$ solution (internal diameter of gas measuring tube 3 mm). End-point 5.08 ml (indicator sodium fluoresceinate 5.12 ml).

Interferences

The sodium hydroxide concentration of the solution to be analysed is rather critical and its optimum depends on the halide content. Pure iodide solutions are best titrated in ammoniacal medium in absence or in presence of only small quantities of sodium hydroxide. Whereas 1 ml of 0.5N NaOH per 5 ml 0.2N iodide solution and 0.5 ml concentrated ammonium hydroxide solution gives good results, the same volume of 5N NaOH reduces the apparent iodide content of the sample to zero. The higher the halide content of the solution, the higher may be the NaOH concentration without leading to destruction of silver iodide. It is advantageous to work at the highest possible NaOH concentration, since it influences favorably the reaction velocity. At equimolecular concentrations the stability of the silver salt in ammoniacal medium against hydrazine at a given concentration of sodium hydroxide diminishes in the following order: CN^-, I^-, Br^-, Cl^-. It seems possible to use this property for the direct individual determination of these ions in their mixtures. For instance, Table II shows that at a slight NaOH alkalinity iodide can be determined in presence of chloride. Anions which form even more soluble silver salts do not interfere.

If the sample contains ions which react with hydrazine in alkaline medium, it must be treated with this substance prior to the titration until, upon further addition of hydrazine, no more gas evolution can be noted. Only those ions interfere which under such conditions are reduced to iodide.

References p. 503.

Titration of cyanide with silver nitrate

Cyanide is usually determined by the complex-formation method of Liebig-Denigès[4], according to which the ammoniacal sample solution, containing potassium iodide as indicator, is titrated with silver nitrate to the first permanent turbidity due to slightly soluble silver iodide.

The gasometric titration method for cyanide differs from the Liebig-Denigès method with respect to the indicator: hydrazine is used instead of iodide. It is based on the fact that the silver of the complex anion $[Ag(CN)_2]^-$ does not react with hydrazine in ammoniacal solution, whereas the cation of silver argentocyanide $Ag[Ag(CN)_2]$ reacts according to reaction 2.

The graphs are of the type shown in Fig. 3. The intersection of the line (abscissa) corresponding to the main reaction (no gas evolution) and the line corresponding to the reaction of the titrant with the indicator (gas evolution) marks the end-point.

Reagents

See *Titration of iodide.*

Procedure 3

Transfer 5.00 to 10.00 ml of the sample solution, which contains cyanide ion, to the titration flask, add concentrated ammonium hydroxide, sodium hydroxide and indicator solutions (see Table III for quantities of reagents). Connect the flask with the buret which contains the silver nitrate solution and titrate following the instructions outlined above.

Interferences

See *Titration of iodide.*

TABLE I

TITRATION OF SILVER NITRATE SOLUTION WITH HYDRAZINE SULFATE SOLUTION

$AgNO_3$ taken		*Additions to the $AgNO_3$ solution*	*$N_2H_4.H_2SO_4$ consumed*			*Δ %*
M	*ml*		*M*	*gasometric titration ml*	*theoretical ml*	
0.2000	5.00	0.5 ml conc. NH_4OH	0.0500	5.02		
0.2000	5.00	*idem*	0.0500	4.99		
0.2000	5.00	*idem* + 1 ml 0.5*N* NaOH	0.0500	4.98		
				mean 4.99	5.00	−0.20
0.1000	5.00	0.5 ml conc. NH_4OH + 1 ml 0.5*N* NaOH	0.0250	5.02		
0.1000	5.00	*idem*	0.0250	5.03		
0.1000	5.00	*idem*	0.0250	4.99		
				mean 5.01	5.00	+0.20
0.0100	5.00	0.1 ml conc. NH_4OH + 1 ml 0.5*N* NaOH	0.0025	5.06		
0.0100	5.00	*idem*	0.0025	4.98		
0.0100	5.00	*idem*	0.0025	5.05		
				mean 5.03	5.00	+0.60

TABLE II

TITRATION OF POTASSIUM IODIDE SOLUTION WITH SILVER NITRATE SOLUTION

KI taken		*Additions to the KI solution*	*$AgNO_3$ consumed*			Δ %
M	*ml*		*M*	*gasometric titration ml*	*with indicator sodium fluoresceinate*[4] *ml*	
0.01	5.00	0.5 ml conc. NH_4OH + 0.2 ml indicator	0.01	5.16		
0.01	5.00	*idem*	0.01	5.12		
0.01	5.00	*idem*	0.01	5.10		
				mean 5.13	mean 5.12	+0.19
0.05	5.00	0.5 ml conc. NH_4OH + 0.7 ml indicator	0.05	5.12		
0.05	5.00	*idem*	0.05	5.08		
				mean 5.10	mean 5.12	−0.39
0.2	5.00	0.5 ml conc. NH_4OH + 2.5 ml indicator $\}$ = A	0.2	5.00		
0.2	5.00	A	0.2	4.99		
0.2	5.00	A	0.2	4.98		
0.2	5.00	A + 1 ml 0.5*N* NaOH	0.2	5.00		
0.2	5.00	*idem*	0.2	5.00		
				mean 4.99	mean 5.00	−0.20
0.2	5.00	0.058 g NaCl A + 1 ml 0.5*N* NaOH	0.2	5.06		+1.20
0.2	5.00	0.116 g NaCl A + 1 ml 0.5*N* NaOH	0.2	5.03		+0.60
0.2	5.00	0.290 g NaCl A + 1 ml 0.5*N* NaOH	0.2	5.05		+1.00
0.2	5.00	0.580 g NaCl A + 1 ml 0.5*N* NaOH	0.2	5.05		+1.00
0.2	5.00	1.160 g NaCl A + 2 ml 0.5*N* NaOH	0.2	5.00		0.00

TABLE III

TITRATION OF POTASSIUM CYANIDE SOLUTION WITH SILVER NITRATE SOLUTION

KCN taken		*Additions to the KCN solution*	*$AgNO_3$ consumed*			Δ %
M	*ml*		*M*	*gasometric titration ml*	*Liebig-Denigès method*[4] *ml*	
0.1	5.00	0.5 ml conc. NH_4OH + 3 ml 0.5*N* NaOH + 1 ml indicator	0.05	4.85		
0.1	5.00	*idem*	0.05	4.80		
0.1	5.00	*idem*	0.05	4.84		
				mean 4.83	mean 4.82	+0.21

ACKNOWLEDGEMENTS

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References p. 503.

SUMMARY

Several argentometric determinations have been worked out to show that the gasometric titration method is applicable not only to acid-base and redox reactions, but also to precipitation and complex-formation reactions. The processes reported allow the direct and indirect determination of iodide and cyanide, as well as the direct titration of silver ion in soluble and slightly soluble silver salts.

RÉSUMÉ

Plusieurs dosages argentométriques ont été élaborés démontrant que la méthode de titration gazométrique n'est pas seulement applicable aux réactions alcali-acidimétriques et aux réactions d'oxydo-réduction, mais qu'elle s'applique également aux réactions par précipitation et par formation de complexes. Les procédés décrits permettent le dosage direct et le dosage indirect des iodures et des cyanures, de même que le titrage direct de l'ion argent dans ses sels solubles ou peu solubles.

ZUSAMMENFASSUNG

Es wurden verschiedene argentometrische Bestimmungen ausgearbeitet, welche zeigen, dass die gasometrische Titrationsmethode nicht nur für Säure-Basen-Reaktionen und für Oxydo-Reduktions-Reaktionen anwendbar ist, sondern auch für Fällungs- und komplexbildende Reaktionen. Die beschriebenen Verfahren erlauben die direkte und die indirekte Bestimmung der Jodide und Cyanide, sowie auch die direkte Titration des Silberions in seinen löslichen oder wenig löslichen Salzen.

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MODIFIED ETHYLENEDIAMINETETRAACETATE METHOD FOR THE DIRECT ESTIMATION OF MAGNESIUM

by

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The use of ethylenediaminetetraacetic acid for the titration of calcium and magnesium is now well established[1]. The end-point is not very sharp however and various attempts have been made to improve it[2,3]. The present authors have adopted WILEY's method[4] for the determination of calcium. The latter is precipitated as molybdate and the magnesium is titrated with EDTA in the filtrate. The sum of the calcium and magnesium can be found first by direct titration. The method is suitable for the routine analysis of dolomite and limestone. Details of the analysis will be published later.

PROCEDURE

A slightly acid solution of a mixture of calcium and magnesium is first diluted to 50 ml and heated to about 80° C and then 5 to 10 ml of 10% ammonium molybdate solution are added and the solution is well stirred for a few minutes. Then 2 ml of NH_4OH-NH_4Cl buffer (pH 10) are added and the solution is boiled for a few minutes. Calcium molybdate precipitates out and the precipitation is complete in the alkaline pH. The solution is allowed to cool and then filtered through a Whatman No. 40 filter paper. The precipitate is washed several times with 10 ml portions of 1:3 alcohol water. The filtrate is then titrated with standard EDTA solution after the addition of 2 ml of NH_4OH-NH_4Cl buffer (pH 10) and 4-6 drops of 0.5% Solochrome Black T indicator solution. The presence of ammonium molybdate does not interfere with the EDTA titration using Solochrome Black T indicator.

SUMMARY

Magnesium and calcium are determined together, using EDTA solution with Solochrome Black T indicator. Calcium is then precipitated out as molybdate and the magnesium is determined in the filtrate.

RÉSUMÉ

Le magnésium et le calcium peuvent être dosés ensemble au moyen d'une solution d'EDTA, en utilisant le noir de solochrome T comme indicateur. Le calcium est alors précipité comme molybdate et le magnésium est ensuite dosé dans le filtrat.

ZUSAMMENFASSUNG

Magnesium und Calcium können zusammen mit EDTA-Lösung und unter Verwendung von Solochrom T Schwarz als Indikator bestimmt werden. Das Calcium wird dann als Molybdat gefällt und das Magnesium im Filtrat bestimmt.

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VOLUMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS

VIII. OXIDATION WITH CERIC SULPHATE FERROUS ETHYLENEDIAMINE SULPHATE METHOD

by

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The salts of quadrivalent cerium are the most versatile of the strong oxidizing agents, which may be used as standard solutions. CARAWAY AND OESPER[1] showed that ferrous ethylenediamine sulphate, $FeSO_4.(CH_2{\cdot}NH_3)_2SO_4.4H_2O$, reacted stoichiometrically with ceric sulphate which is commonly employed in oxidimetric titrations.

In acid medium ceric sulphate reacts with ferrous ammonium sulphate, cuprous chloride, potassium thiocyanate, sodium thiosulphate, sodium nitrite, hydrogen peroxide, sodium oxalate, hydroquinone and pyruvic acid in accordance with the equations:

$$\begin{array}{lcl}
Ce^{+4} + Fe^{+2} & \rightarrow & Ce^{+3} + Fe^{+3} \\
2Ce^{+4} + Cu_2^{+2} & \rightarrow & 2Ce^{+3} + 2Cu^{+2} \\
6Ce^{+4} + CNS^- + 4\,H_2O & \rightarrow & 6Ce^{+3} + CN^- + SO_4^{-2} + 8H^+ \\
2Ce^{+4} + 2S_2O_3^{-2} & \rightarrow & 2Ce^{+3} + S_4O_6^{-2} \\
2Ce^{+4} + NO_2^- + H_2O & \rightarrow & 2Ce^{+3} + NO_3^- + 2H^+ \\
2Ce^{+4} + O_2^{-2} & \rightarrow & 2Ce^{+3} + O_2 \\
2Ce^{+4} + C_2O_4^{-2} & \rightarrow & 2Ce^{+3} + 2CO_2 \\
2Ce^{+4} + C_6H_4(OH)_2 & \rightarrow & 2Ce^{+3} + C_6H_4O_2 + 2H^+ \\
2Ce^{+4} + CH_3COCOOH + H_2O & \rightarrow & 2Ce^{+3} + CH_3COOH + CO_2 + 2H^+
\end{array}$$

In the present investigation the substances have been determined indirectly by a volumetric method using ceric sulphate as oxidizing agent. The excess of standard ceric sulphate added to each of the substances was titrated with standard ferrous ethylenediamine sulphate solution using ferroin as an indicator.

EXPERIMENTAL

A known weight of each substance was mixed with an excess of standard ceric sulphate solution and the mixture acidified with sulphuric acid to keep its normality between 1 and 2*N*. In case of potassium thiocyanate the normality of the mixture with respect to sulphuric acid was kept between 4 and 6*N*. The mixtures containing sodium nitrite, sodium oxalate, hydroquinone and pyruvic acid were warmed to about 60° C, and the mixtures containing cuprous chloride and potassium thiocyanate were heated for about ten minutes and then allowed to cool. In each case the excess of ceric sulphate was titrated against standard ferrous ethylenediamine sulphate solution using ferroin as an indicator.

Ceric sulphate was standardized with ferrous ethylenediamine sulphate (FES) which was prepared by the method of CARAWAY and OESPER *(loc. cit.)*.

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[1] KATHRYN P. CARAWAY AND RALPH E. OESPER, *J. Chem. Educ.*, 24 (1947) 235.

The results given in Tables I to IX show that the substances can be determined indirectly by the volumetric method, using ceric sulphate as an oxidizing agent in acid medium.

TABLE I

FERROUS AMMONIUM SULPHATE

$FeSO_4.(NH_4)_2SO_4.6H_2O$ taken (g)	N/20 $Ce(SO_4)_2$ added (ml)	N/20 FES used for excess $Ce(SO_4)_2$ (ml)	N/20 $Ce(SO_4)_2$ used by $FeSO_4.(NH_4)_2SO_4.6H_2O$ (ml)	$FeSO_4.(NH_4)_2SO_4.6H_2O$ found (g)
0.0980	10.00	5.00	5.00	0.0981
0.1980	20.00	9.90	10.10	0.1981
0.2950	25.00	9.95	15.05	0.2951
0.3932	30.00	9.95	20.05	0.3932
0.4902	40.00	15.00	25.00	0.4903

TABLE II

CUPROUS CHLORIDE

Cu_2Cl_2 taken (g)	N/20 $Ce(SO_4)_2$ added (ml)	N/20 FES used for excess $Ce(SO_4)_2$ (ml)	N/20 $Ce(SO_4)_2$ used by Cu_2Cl_2 (ml)	Cu_2Cl_2 found (g)
0.0247	20.00	15.00	5.00	0.0248
0.0494	20.00	10.00	10.00	0.0495
0.0740	20.00	5.00	15.00	0.0742
0.0989	30.00	10.00	20.00	0.0990
0.1136	43.00	20.00	23.00	0.1138

TABLE III

POTASSIUM THIOCYANATE

KCNS taken (g)	N/20 $Ce(SO_4)_2$ added (ml)	N/20 FES used for excess $Ce(SO_4)_2$ (ml)	N/20 $Ce(SO_4)_2$ used by KCNS (ml)	KCNS found (g)
0.0040	10.00	5.00	5.00	0.0041
0.0080	20.00	9.90	10.10	0.0082
0.0121	30.00	15.00	15.00	0.0121
0.0160	35.00	15.00	20.00	0.0162
0.0201	40.00	15.00	25.00	0.0202

TABLE IV

SODIUM THIOSULPHATE

$Na_2S_2O_3.5H_2O$ taken (g)	N/20 $Ce(SO_4)_2$ added (ml)	N/20 FES used for excess $Ce(SO_4)_2$ (ml)	N/20 $Ce(SO_4)_2$ used by $Na_2S_2O_3.5H_2O$ (ml)	$Na_2S_2O_3.5H_2O$ found (g)
0.0632	10.00	4.90	5.10	0.0633
0.1245	20.00	9.95	10.05	0.1247
0.1740	25.00	10.95	14.05	0.1744
0.2478	35.00	15.00	20.00	0.2482
0.3098	37.00	12.00	25.00	0.3103

TABLE V

SODIUM NITRITE

$NaNO_2$ *taken* (g)	*N/20* $Ce(SO_4)_2$ *added* (ml)	*N/20 FES used for excess* $Ce(SO_4)_2$ (ml)	*N/20* $Ce(SO_4)_2$ *used by* $NaNO_2$ (ml)	$NaNO_2$ *found* (g)
0.0140	15.00	6.80	8.20	0.0141
0.0204	20.00	8.10	11.90	0.0205
0.0258	25.00	10.00	15.00	0.0259
0.0327	35.00	16.00	19.00	0.0328
0.0396	40.00	17.00	23.00	0.0397

TABLE VI

HYDROGEN PEROXIDE

H_2O_2 *taken* (g)	*N/20* $Ce(SO_4)_2$ *added* (ml)	*N/20 FES used for excess* $Ce(SO_4)_2$ (ml)	*N/20* $Ce(SO_4)_2$ *used by* H_2O_2 (ml)	H_2O_2 *found* (g)
0.0035	15.00	11.00	4.00	0.0034
0.0102	20.00	7.90	12.10	0.0103
0.0137	30.00	13.70	16.30	0.0138
0.0171	35.00	14.60	20.40	0.0173
0.0213	45.00	19.80	25.20	0.0214

TABLE VII

SODIUM OXALATE

$(COONa)_2$ *taken* (g)	*N/20* $Ce(SO_4)_2$ *added* (ml)	*N/20 FES used for excess* $Ce(SO_4)_2$ (ml)	*N/20* $Ce(SO_4)_2$ *used by* $(COONa)_2$ (ml)	$(COONa)_2$ *found* (g)
0.0240	15.00	7.80	7.20	0.0241
0.0334	20.00	10.00	10.00	0.0335
0.0498	30.00	15.10	14.90	0.0499
0.0670	35.00	15.00	20.00	0.0670
0.0835	45.00	20.05	24.95	0.0836

TABLE VIII

HYDROQUINONE

$C_6H_4(OH)_2$ *taken* (g)	*N/20* $Ce(SO_4)_2$ *added* (ml)	*N/20 FES used for excess* $Ce(SO_4)_2$ (ml)	*N/20* $Ce(SO_4)_2$ *used by* $C_6H_4(OH)_2$ (ml)	$C_6H_4(OH)_2$ *found* (g)
0.0138	10.00	4.95	5.05	0.0139
0.0275	20.00	9.95	10.05	0.0276
0.0412	25.00	10.00	15.00	0.0413
0.0548	30.00	10.00	20.00	0.0550
0.0686	40.00	15.00	25.00	0.0688

TABLE IX

PYRUVIC ACID

$CH_3COCOOH$ taken (g)	N/20 $Ce(SO_4)_2$ added (ml)	N/20 FES used for excess $Ce(SO_4)_2$ (ml)	N/20 $Ce(SO_4)_2$ used by $CH_3COCOOH$ (ml)	$CH_3COCOOH$ found (g)
0.0109	10.00	5.00	5.00	0.0110
0.0218	20.00	10.00	10.00	0.0220
0.0327	30.00	15.05	14.95	0.0329
0.0440	35.00	15.00	20.00	0.0440
0.0528	45.00	21.00	24.00	0.0528

SUMMARY

Ceric sulphate has been used as an oxidizing agent in acid medium for the indirect volumetric determinations of ferrous ammonium sulphate, cuprous chloride, potassium thiocyanate, sodium thiosulphate, sodium nitrite, hydrogen peroxide, sodium oxalate, hydroquinone and pyruvic acid. The excess of ceric sulphate added to each of the substances in acid medium was titrated with standard ferrous ethylenediamine sulphate solution using ferroin as an indicator.

RÉSUMÉ

Le sulfate de cérium(IV) peut être utilisé comme oxydant, en milieu acide, pour le dosage volumétrique indirect du sulfate de fer(II) et d'ammonium, du chlorure de cuivre(I), du thiocyanate de potassium, du thiosulfate de sodium, du nitrite de sodium, du peroxyde d'hydrogène, de l'oxalate de sodium, de l'hydroquinone et de l'acide pyruvique. L'excès de sulfate de cérium(IV) ajouté à chacune de ces substances, en milieu acide, est titré avec une solution de sulfate de fer(II) et d'éthylènediamine, en présence de ferroïne comme indicateur.

ZUSAMMENFASSUNG

Cer(IV)sulfat wurde in saurem Medium als Oxydationsmittel für die indirekten volumetrischen Bestimmungen von Ammoniumferrosulfat, Kupfer(I)chlorid, Kaliumthiocyanat, Natriumthiosulfat, Natriumnitrit, Wasserstoffperoxyd, Natriumoxalat, Hydrochinon und Brenztraubensäure verwendet. Der Überschuss an Cer(IV)sulfat, der jeder der oben aufgeführten Substanzen in saurem Medium zugesetzt wurde, lässt sich mit eingestellter Eisen(II)äthylendiaminsulfatlösung zurücktitrieren. Ferroin dient dabei als Indikator.

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DETERMINATION OF THIOUREA AND TETRAMETHYLTHIOUREA
AN IODINE-ARSENITE METHOD

by

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CUTHILL AND ATKINS[1] studied the oxidation of thiourea by alkaline iodine and adopted this reaction for the quantitative determination of thiourea:

$$CS(NH_2)_2 + 10\ NaOH + 4\ I_2 \rightarrow CO(NH_2)_2 + Na_2SO_4 + 8\ NaI + 5\ H_2O.$$

An aqueous solution of thiourea was mixed with an equal volume of $2N$ sodium hydroxide to which a measured excess of standard iodine solution was added. After 15 minutes the system was acidified with $4N$ sulphuric acid and the unreacted iodine titrated with standard thiosulphate. However, the accuracy of results obtained by their procedure depended on various factors such as the order of mixing, duration of standing and the concentration of iodine and alkali. These observations emphasized the necessity for a reinvestigation of the CUTHILL-ATKINS method. The present work presents a modified procedure for determining thiourea depending on the titration of excess iodine with standard As_2O_3 in the appropriate pH range. Conditions and results are also recorded for the determination of tetramethylthiourea.

EXPERIMENTAL

A stock solution of thiourea was prepared by dissolving an accurately weighed quantity of E. Merck's guaranteed reagent in water. Tetramethylthiourea was prepared starting from tetramethylthiuram disulphide[2]. The purified product melted at 78° C and its aqueous solution was obtained by dissolving an exactly weighed quantity in water.

To an aliquot of the thiourea solution in a glass-stoppered Erlenmeyer flask were added sufficient sodium hydroxide to maintain an overall normality of 1 to $3N$ and a measured excess of iodine solution. The contents of the flask were swirled and set aside in ice-cold water for about 30 minutes. The alkali was just neutralized with $2N$ HCl or H_2SO_4 and the pH of the system raised by introducing an excess of borax-boric acid buffer. The buffer solution was prepared by dissolving 8 g and 4 g of crystallized borax and pure boric acid respectively in 100 ml of water[3]. The unreacted iodine was then titrated with $0.1N$ arsenious oxide solution to the usual starch end-point[4]. The difference in the initial and final titre values of As_2O_3 corresponds to the quantity of iodine consumed and hence to the amount of thiourea present in the system in accordance with the following equations:

$$8\ NaOH + 4\ I_2 \rightarrow 4\ NaIO + 4\ NaI + 4\ H_2O \quad (1)$$
$$CS(NH_2)_2 + 4\ NaIO + H_2O \rightarrow CO(NH_2)_2 + 4\ NaI + H_2SO_4 \quad (2)$$
$$2\ As_2O_3 + 4\ I_2 + 4\ H_2O \rightarrow 2\ As_2O_5 + 8\ HI \quad (3)$$

Thus $1\ CS(NH_2)_2 \equiv 4\ I_2 \equiv 2\ As_2O_3$, or in other words, 1 ml of $1N$ As_2O_3 corresponds to 0.009500 g of thiourea. A representative set of results is given in Table I. It includes also the values obtained by thiosulphate titrations.

TABLE I

Overall normality of NaOH = 1-3N

Expt. No.	Vol. of thiourea taken (ml)	Vol. of iodine added (ml)	Vol. of 0.1N $Na_2S_2O_3$ (ml)			Vol. of 0.1N As_2O_3 (ml)			$(NH_2)_2CS$ (g)			Error %	
			$= I_2$ added	$= I_2$ unreacted	$= I_2$ reacted	$= I_2$ added	$= I_2$ unreacted	$= I_2$ reacted	By weight (x)	By thio (a)	By As_2O_3 (b)	(a)	(b)
1	10.0	20.0	20.20	16.00	4.20	20.20	16.00	4.20	0.00399	0.003989	0.003989	0.025	0.025
2	20.0	25.0	25.25	16.85	8.40	25.25	16.85	8.40	0.00798	0.007978	0.007978	0.025	0.025
3	10.0	30.0	30.30	13.55	16.75	30.30	13.55	16.75	0.01596	0.01592	0.01592	0.25	0.25
4	20.0	60.0	60.60	27.20	33.40	60.60	27.10	33.50	0.03192	0.03173	0.03182	0.66	0.33
5	25.0	70.0	70.70	28.95	41.75	70.70	28.80	41.90	0.03990	0.03966	0.03980	0.60	0.25
6	30.0	90.0	90.90	40.65	50.25	90.90	40.60	50.30	0.04788	0.04773	0.04778	0.31	0.20
7	40.0	100.0	101.0	34.00	67.00	101.0	33.90	67.10	0.06384	0.06365	0.06374	0.32	0.16

TABLE IV

Overall normality of NaOH = ∿ 0.4N

Expt. No.	Vol. of $(NMe_2)_2CS$ taken (ml)	Vol. of iodine added (ml)	Vol. of 0.1N $Na_2S_2O_3$ (ml)			Vol. of 0.1N As_2O_3 (ml)			$(NMe_2)_2CS$ (g)			Error %	
			$= I_2$ added	$= I_2$ unreacted	$= I_3$ reacted	$= I_2$ added	$= I_2$ unreacted	$= I_3$ reacted	By weight (x)	By thio (a)	By As_2O_3 (b)	(a)	(b)
1	20.0	10.0	10.10	5.10	5.00	10.10	5.15	4.95	0.008200	0.008250	0.008168	0.62	0.40
2	10.0	20.0	20.20	10.20	10.00	20.20	10.20	10.00	0.01640	0.01650	0.01650	0.62	0.62
3	20.0	30.0	30.30	10.40	19.90	30.30	10.40	19.90	0.03280	0.03284	0.03284	0.12	0.12
4	25.0	40.0	40.40	15.40	25.00	40.40	15.50	24.90	0.04100	0.04125	0.04109	0.61	0.22
5	30.0	40.0	40.40	10.55	29.85	40.40	10.55	29.85	0.04920	0.04925	0.04925	0.10	0.10
6	40.0	50.0	50.50	10.70	39.80	50.50	10.70	39.80	0.06560	0.06567	0.06567	0.10	0.10

Tetramethylthiourea was determined by adopting the above experimental procedure but maintaining the total sodium hydroxide concentration in the system between 0.1 and 0.6*N*. The reaction may be expressed as follows:

$$CS(NMe_2)_2 + 4\ NaIO + H_2O \rightarrow CO(NMe_2)_2 + 4\ NaI + H_2SO_4 \quad \ldots\ldots\ldots\ldots \quad (4)$$

It therefore follows that 1 $CS(NMe_2)_2 = 4\ I_2 = 2\ As_2O_3$, or, in other words 1 ml of 1*N* As_2O_3 is equal to 0.01650 g of tetramethylthiourea. Results for a typical series of experiments are given in Table IV which also includes the values obtained by the thiosulphate method.

TABLE II

EFFECT OF NaOH CONCENTRATION

Volume of thiourea = 10 ml. Iodine added = 30 ml. Reaction time = 30 minutes

Expt. No.	*Overall normality of NaOH (N)*	*Volume of 0.1N As_2O_3 (ml)*			*$(NH_2)_2CS$ (g)*		*Error %*
		= I_2 added	*= I_2 unreacted*	*= I_2 reacted*	*Weighed*	*Calcd.*	
1	0.4	30.30	13.70	16.60	0.01596	0.01577	—1.2
2	0.8	30.30	13.65	16.65	0.01596	0.01581	—0.93
3	1.0	30.30	13.55	16.75	0.01596	0.01592	—0.25
4	1.5	30.30	13.55	16.75	0.01596	0.01592	—0.25
5	2.0	30.30	13.55	16.75	0.01596	0.01592	—0.25
6	2.5	30.30	13.55	16.75	0.01596	0.01592	—0.25
7	3.0	30.30	13.55	16.75	0.01596	0.01592	—0.25

TABLE III

EFFECT OF IODINE CONCENTRATION

Volume of thiourea = 20 ml. Overall normality of NaOH = 1*N*. Reaction times = 30 minutes

Expt. No.	*Vol. of iodine added (ml)*	*Volume of 0.1N As_2O_3 (ml)*			*$(NH_2)_2CS$ (g)*		*Error %*
		= I_2 added	*= I_2 unreacted*	*= I_2 reacted*	*weighed*	*calcd.*	
1	40.0	40.40	7.30	33.10	0.03192	0.03145	—1.5
2	50.0	50.50	17.30	33.20	0.03192	0.03154	—1.2
3	60.0	60.60	27.10	33.50	0.03192	0.03182	—0.31
4	80.0	80.80	47.30	33.50	0.03192	0.03182	—0.31
5	100.0	101.0	67.50	33.50	0.03192	0.03182	—0.31

TABLE V

EFFECT OF NaOH CONCENTRATION

Volume of tetramethylthiourea = 10 ml. Iodine added = 20 ml. Reaction time = 30 minutes

Expt. No.	*Overall normality of NaOH (N)*	*Volume of 0.1N As_2O_3 (ml)*			*$(NMe_2)_2CS$ (g)*		*Error %*
		= I_2 added	*= I_2 unreacted*	*= I_2 reacted*	*weighed*	*calcd.*	
1	0.1	20.20	10.20	10.00	0.01640	0.01650	+0.62
2	0.2	20.20	10.20	10.00	0.01640	0.01650	+0.62
3	0.3	20.20	10.20	10.00	0.01640	0.01650	+0.62
4	0.4	20.20	10.20	10.00	0.01640	0.01650	+0.62
5	0.6	20.20	10.20	10.00	0.01640	0.01650	+0.62
6	0.9	20.20	10.10	10.10	0.01640	0.01666	+1.6
7	1.2	20.20	10.00	10.20	0.01640	0.01683	+2.6

TABLE VI

EFFECT OF IODINE CONCENTRATION

Volume of tetramethylthiourea = 10 ml. Overall normality of NaOH = 0.4N
Reaction time = 30 minutes

Expt. No.	*Vol. of iodine added (ml)*	*Volume of 0.1N As_2O_3 (ml)*			*$(NMe_2)_2CS$ (g)*		*% Error*
		= I_2 added	*= I_2 unreacted*	*= I_2 reacted*	*weighed*	*calcd.*	
1	15.0	15.15	5.25	9.90	0.01640	0.01633	−0.44
2	20.0	20.20	10.20	10.00	0.01640	0.01650	+0.62
3	30.0	30.30	20.30	10.00	0.01640	0.01650	+0.62
4	40.0	40.40	30.40	10.00	0.01640	0.01650	+0.62
5	50.0	50.50	40.50	10.00	0.01640	0.01650	+0.62

DISCUSSION

When iodine solution, followed by sodium hydroxide, was added to thiourea, low results were obtained owing to the formation of formamidine disulphide and/or the subsequent precipitation of sulphur. This inherent error was negligible when the addition of alkali preceeded that of iodine (*cf.* EXPERIMENTAL). Incidentally these observations confirm the earlier findings of CUTHILL AND ATKINS[1].

Experiments performed with varying quantities of sodium hydroxide revealed that the oxidation of thiourea by iodine was quantitative over a fairly wide range of alkali concentration (*cf.* Table II). However, normalities below 1N yielded results about 1% low. Although less than twice the theoretical amount of iodine was insufficient for quantitative oxidation of thiourea, a large excess was found to have little adverse effect on the accuracy of the results (*cf.* Table III). Furthermore, the reaction stoichiometry remained unaltered even when the duration of standing exceeded 30 minutes. Hence the optimum conditions for the accurate determination of thiourea are: (1) overall alkalinity of the system between 1 and 3N, (2) 2 to 3-fold excess iodine and a reaction time of about 30 minutes. The present method thus affords the determination of 0.004 to 0.064 g of thiourea in a single operation.

The tetramethylthiourea-iodine reaction proceeds according to equation (4) in an overall sodium hydroxide concentration between 0.1 and 0.6N (*cf.* Table V). Normalities above 0.6N invariably gave high results. The iodine concentration was not critical provided a sufficient excess was maintained (*cf.* Table VI). Under these initial operative conditions the method provides an excellent means of determining 0.008 to 0.06 g of tetramethylthiourea.

It is well known that the reversible reaction between iodine and arsenious oxide, $As_2O_3 + 2\,I_2 + 2\,H_2O \rightleftarrows As_2O_5 + 4\,HI$, proceeds in the forward direction when the hydriodic acid is removed as soon as it is formed. This is usually accomplished by buffers like NaH_2PO_4-Na_2HPO_4, $NaHCO_3$-CO_2 or borax-boric acid in the pH range 4-11[5,6]. Free alkalies, owing to their secondary reactions with iodine, are not recommended for this purpose. In the present work a mixture of borax and boric acid was preferred, since phosphate buffer was slow and inconvenient, and sodium bicarbonate generally caused a partial loss of iodine due to the evolution of carbon dioxide on acidification. It may be mentioned that the present method of determining

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thiourea and tetramethylthiourea is simpler than that of CUTHILL AND ATKINS, and offers an additional advantage of using a primary standard, As_2O_3.

Further work on the reactions involved in the oxidation of thiourea and its derivatives by iodine in weakly alkaline medium and their adaptibility to direct titration using chemical indicator and/or electrometric end-points is now in progress.

The author extends his grateful thanks to Professor S. S. JOSHI for research facilities.

SUMMARY

Oxidation of thiourea and tetramethylthiourea by alkaline iodine is studied. The reaction is found to proceed quantitatively over a wide range of experimental conditions. A method of estimating thiourea and its tetramethyl derivative is developed, based on the titration of the excess iodine against standard arsenious oxide in a suitable pH range.

RÉSUMÉ

Une étude a été effectuée sur l'oxydation de la thiourée et de la tétraméthylthiourée par l'iode, en solution alcaline. La réaction est quantitative dans des conditions expérimentales variées. Une méthode est proposée pour le dosage de la thiourée et de la tétraméthylthiourée; elle est basée sur le titrage de l'iode ajouté en excès, au moyen d'anhydride arsénieux, à un pH convenable.

ZUSAMMENFASSUNG

Es wurde eine Untersuchung ausgeführt über die Oxydation von Thioharnstoff und Tetramethylthioharnstoff mit Jod in alkalischer Lösung. Die Reaktion ist bei verschiedenen Versuchsbedingungen quantitativ. Es wird eine Methode für die Bestimmung von Thioharnstoff und Tetramethylthioharnstoff vorgeschlagen; sie basiert auf der Titration des im Überschuss zugefügten Jods mittels arseniger Säure bei einem geeigneten pH.

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A RAPID AND PRECISE METHOD FOR THE DETERMINATION OF OXYGEN IN CERTAIN GASES

MODIFIED BRADY METHOD

by

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INTRODUCTION

The extended use of experimental systems involving liquid metals occasions continued interest in the oxygen-content of the inactive gases which are to be used to blanket such systems.

Instruments which utilize physicochemical properties have been designed for determination of oxygen in gases. The Beckman oxygen analyser based on the theory of PAULING's[1] Oxygen Meter depends on the paramagnetic nature of oxygen. A method described by PEPKOWITZ[2] converts the oxygen to water and measures the dew point. Such methods, while rapid in response, are not sensitive to minute quantities of oxygen such as one part per million or less.

A diversity of colorimetric methods for the determination of small amounts of oxygen in gas have been proposed. One of the most sensitive methods for small amounts of oxygen is that of WINKLER[3] in which oxygen is absorbed into neutral or alkaline manganous solution and then determined as iodine. WINSLOW AND LIEBHAFSKY[4] adapted this method to determine small quantities of oxygen in gases. PEPKOWITZ[5] adapted the method further, permitting the analysis of small quantities of gas (one liter or less) with a precision of at least one ppm oxygen. By using a modified vacuum technique and by using purer and more sensitive reagents SILVERMAN AND BRADSHAW[6] improved the precision of the method to ±0.33 part per million oxygen.

This colorimetric method is sensitive to small amounts of oxygen of one microliter or less and thus can be used to analyse small quantities of gas, such as one liter. Its disadvantage lies in the time (four hours) involved in completing one analysis. Several samples can be run concurrently but the maximum number of determinations which can be done by one operator is four per day.

BRADY[7] described a very satisfactory apparatus which requires larger volumes of sample gas to determine one part per million of oxygen. In this method oxygen is absorbed into an alkaline solution of sodium anthraquinone-beta-sulfonate, which changes the solution from red to colorless. The course of oxidation is followed by observing the decrease in absorbance using a green filter in a photoelectric colorimeter.

The Brady method was modified as follows so as to be suitable for the determinations of still lower oxygen-concentrations and to obtain greater accuracy and precision:

Tygon joints were eliminated to prevent oxygen diffusion.

Flexibility was attained by the use of ball and socket joints held together firmly by spring clamps.

A more efficient gas-liquid pumping system was used, permitting greater sensitivity to small amounts of oxygen.

A Beckman model DU spectrophotometer was used in place of a Klett colorimeter.

The last two modifications extended the lower limit of detection to 0.005 part per million oxygen. The reported range of the Brady[7] method was 1 to 100 parts per million. The precision of the method was improved by calculating the oxygen-concentration from the slope of the absorbance-change rather than from the difference in absorbance (Brady's method) between two arbitrary points. The optical response of a Beckman-type spectrophotometer is necessary equipment for precision analysis.

The accuracy of the method was enhanced by using an improved method for the de-oxidation of the helium gas in order to obtain a very low oxygen-content carrier-gas for calibration.

APPARATUS

The modified apparatus used is shown schematically in Fig. 1. Ball and socket joints were placed at strategic points to promote flexibility and to permit ready disassembly of the system for cleaning and repair.

Previous experimental work in this laboratory has shown that oxygen can diffuse through

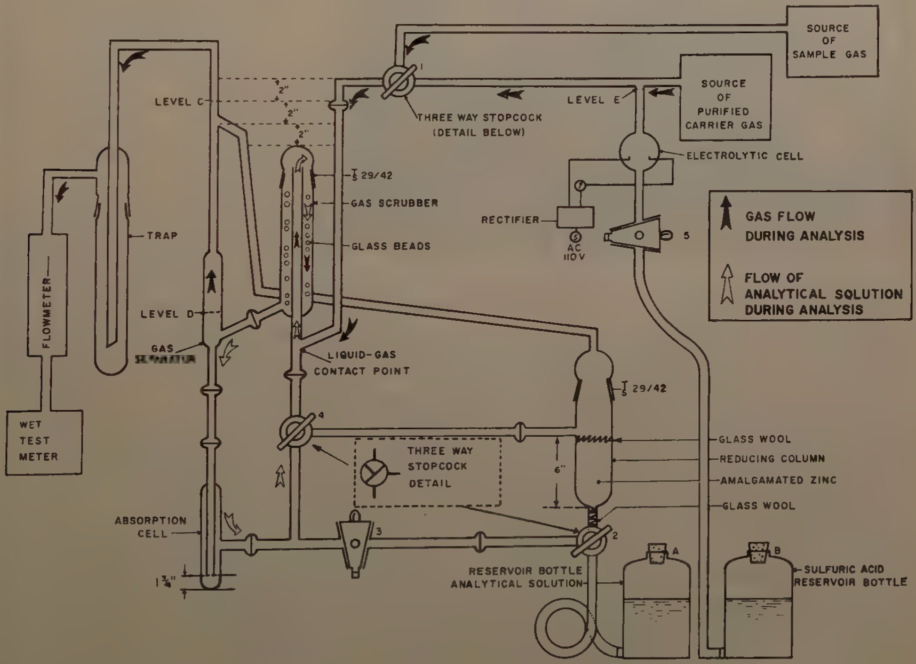

Fig. 1. Schematic of modified Brady apparatus for oxygen analysis.

tygon tubing; for this reason tygon is not used in the system except as hose connections to the reservoir bottles. This is permissible since this part of the system is cut off from the stream of gas flow during the course of the analysis.

In preparation, the analytical solution is passed through a reducing column containing amalgamated zinc and then the solution is ready to be circulated through the analytical portion of the system.

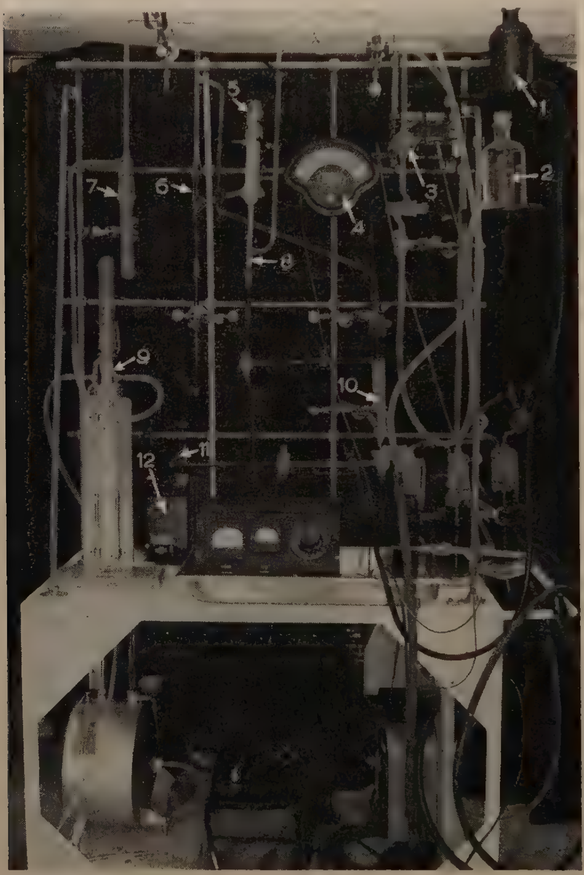

Fig. 1A.

1 Reservoir bottle (anal. solution)
2 Reservoir bottle (sulphuric acid)
3 Electrolytic cell
4 Milliammeter
5 Scrubber
6 Gas separator
7 Trap
8 Liquid gas contact point
9 Flow meter
10 Reducing column
11 Absorption cell
12 Beckman spectrophotometer

Sample gas is passed through a gas-scrubber in such a way that it pumps the analytical solution through the system. From the gas-scrubber it passes to a gas separator where the liquid and gas are separated. The gas passes out of the system by way of a trap for excess moisture, through a flow meter, and through a wet test meter which records the total amount of sample-gas.

The analytical solution passes from the gas separator into an absorption cell and back up into the gas-scrubber. The absorbance of the solution is determined at regular intervals by means of a Beckman model DU spectrophotometer. The absorption cell is mounted permanently in the spectrophotometer for an extended series of analyses.

The reservoir bottle containing the analytical solution is covered with black tape to prevent deterioration of the solution by light. The rest of the system is partially covered with black tape. "Peep-holes" are left to permit observation of the pumping action and the color of the solution. The area of the absorption cell immediately above the spectrophotometer unit is completely covered with black tape to prevent stray light interfering with absorbance readings.

The details of the gas-scrubber section are shown in Fig. 2A. The dimensions are critical in order to obtain maximum pumping efficiency. The sample gas enters through 8-mm glass tubing and is deflected by a piece of 4-mm glass tubing into the analyticalsloution. The gas forces some liquid up the 4-mm tubing, but the 4-mm and 8-mm tubing are sealed together strategically, as shown, to prevent liquid and gas passing up between them. From the top of this tubing the

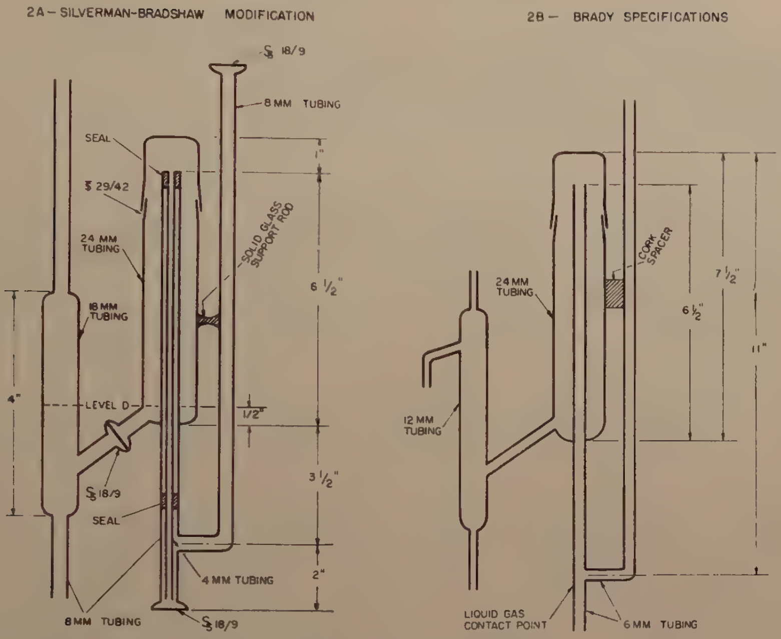

Fig. 2. Details of gas-scrubber
2A-SILVERMAN-BRADSHAW modification
2B-Brady specifications

liquid splashes into a 24-mm section filled with glass beads in order to obtain maximum mixing action. Both gas and liquid pass into the 18-mm liquid-gas separator.

In order to calibrate the system, oxygen is generated in an electrolytic cell (Fig. 3). The cell consists of a 50-ml bulb with tungsten wire-leads inserted into the glass. The current source is a 110-volt 60-cycle supply put through a rectifying control unit which converts the alternating current input to low amperage (6 milliamperes) direct current. The current is read on a 0 to 25 milliammeter accurate to one percent.

In order to obtain a carrier-gas low in oxygen-content for calibration, NaK bubblers containing 700 to 5,000 ml of liquid NaK eutectic (78 percent potassium) were used. (A compact NaK bubbler to be used for laboratory experiments is currently in process of design.)

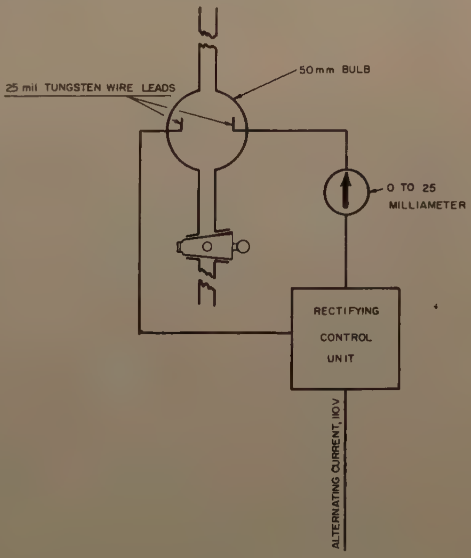

Fig. 3. Details of electrolytic cell.

REAGENTS

Scrubbing solution, analytical reagent. Dissolve 0.033 g of sodium anthraquinone-beta-sulfonate in 300 ml of distilled water by heating gently. Cool the solution to room temperature. Add 10 ml of 30 percent sodium hydroxide solution by pipette, then dilute to 500-ml volume with water. Do not use the reagent when it is more than 2 weeks old. Store in a brown bottle.

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Amalgamated zinc, granular (or shot). Stir 400 g of 20-mesh granular zinc (or zinc shot) with 400 ml of mercuric chloride solution (5 g per 100 ml) for ten minutes. Drain off the excess mercuric chloride solution and thoroughly wash the amalgamated zinc with distilled water. (When the granular zinc amalgam has become spent it can be regenerated in places in the reducing column. Wash first with 100 ml of (1 to 4) HCl, then continue washing with distilled water until the wash water is neutral.)

Oxygen-free carrier-gas can be obtained by either of two methods:
1) Put tank helium which may contain from 2 to 20 parts per million oxygen, through a bubbler containing 200 ml of liquid NaK eutectic at a flow rate of less than 250 ml per minute. This method reduces the oxygen concentration to approximately 0.1 part per million or less.
2) Put tank hydrogen, containing 2 to 5 parts per million oxygen, through a series of three gas washing bottles (300 ml size). Each should contain 130 grams of analgamated zinc shot (see above) plus 200 ml of purifying scrubbing solution (see below). Cover each wash bottle with black tape. The effluent oxygen-concentration should be from 0.3 to 0.5 part per million.

The first method is preferable as it produces the more constant results and permits lower oxygen-concentration in the carrier gas.

Scrubbing solution, purifying grade. Dissolve 1.5 g sodium anthraquinone-beta sulfonate in 600 ml water, with gentle heat. Cool the solution to room temperature. Add 20 ml of 30 per cent sodium hydroxide, by pipette. Dilute to one liter with distilled water. This solution can be stored in a dark bottle for 60 days.

Sulfuric acid solution. Add 10 g of concentrated sulfuric acid to 90 ml of distilled water.

PROCEDURE

Assemble the system as shown in Fig. 1 with the granulated zinc amalgam in place and with freshly prepared sodium-anthraquinone-beta-sulfonate solution, analytical reagent, in reservoir bottle A. Turn stop-cock 1 so that oxygen-free carrier-gas can flow through the system. Purge the system for 10 minutes with oxygen-free gas, rotating stop-cocks 2, 3 and 4 so that the entire system is flushed with oxygen-free gas.

Preparation of the reduced analytical solution

Shut off the carrier gas, turn stop-cock 2 so that the analytical solution can flow up through the reducing column. Shut stop-cock 3 and open stop-cock 4 between the gas-scrubber and the reducing column. Raise the level of reservoir bottle A until the entire system is filled with liquid up to level C. Open stop-cock 3 and allow the analytical solution to drain back into the reservoir bottle via stop-cocks 3 and 2. Repeat this series of operations until the analytical solution is homogeneous in color and no more gas bubbles remain (3 to 5 times should be sufficient). Adjust the liquid to level D. This level should be marked, as deviation from it affects the calibration factor.

Circulation of sample gas

To start the test, turn stop-cocks 3 and 4 so that the analytical solution can circulate only through the following path: from the gas-scrubber through the gas-separator, absorption cell and back to the gas-scrubber. Turn stop-cock 1 so that the sample gas passes into the gas-scrubber through the gas-separator into the flow meter and out through the wet-test meter. Adjust the rate of gas-flow, as measured by the flow meter, so that the flow ranges from 100 to 300 ml per minute. A flow rate of 250 ml per minute is optimum for gases containing 1 part per million oxygen or less. A flow-rate of 100 ml per minute is optimum for gases containing 1 to 15 parts per million oxygen.

Determination of analytical plot

Simultaneously record the volume of gas (in liters) from the wet-test meter and the absorbance at 530 mμ with a slit-width of 0.04. Take readings at intervals of 5 to 10 minutes if the oxygen concentration is one part per million or less; take readings every one to two minutes if the oxygen-concentration is 1 to 15 parts per million.

Follow the course of analysis by plotting the absorbance as ordinate and the volume of gas as abscissa. The points should approach a straight line after a few readings. If the oxygen concentration is less than 1 part per million, continue the analysis until 10 to 20 liters of gas have been monitored and the plotted points form a straight line. If the oxygen concentration is 1 to 15 parts per million, continue the analysis until 2 to 6 liters of gas have been monitored and the plotted points form a straight line. Fig. 5 shows typical plots for analyses ranging from 0.2 to 8 parts per million.

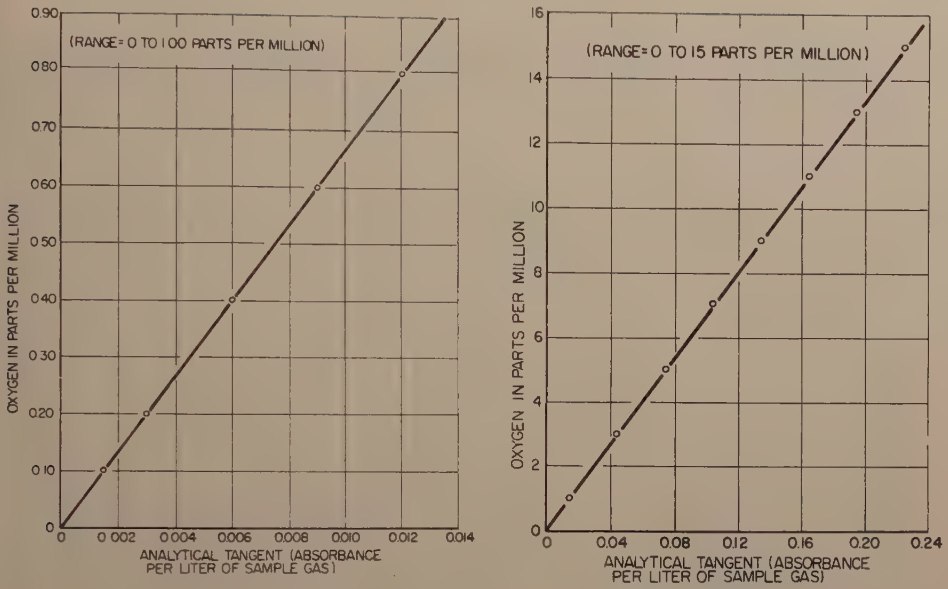

Fig. 4. Calibration curves (oxygen in parts per million *versus* analytical tangent).

Calculation of oxygen concentration

Calculate the corrected analytical tangent of the analytical plot as follows:

$$\text{Analytical tangent (absorbance per liter)} = \frac{\Delta A}{\Delta V} \ldots \text{Eq. 1}$$

Where ΔA = the change in absorbance observed between points A and B,

ΔV = the difference in gas volume, in liters, between points, A and B, corrected to standard conditions.

Refer to a calibration plot (Fig. 4) and read the oxygen concentration in parts per million. For example, the oxygen-concentration of sample B, Fig. 5, was calculated as follows:

$$\Delta A = 1.890\text{-}1.550 = 0.340$$

$$\Delta V = (7\text{-}0) \cdot \frac{273}{298} \cdot \frac{761}{760} = 6.4$$

$$\frac{\Delta A}{\Delta V} = \frac{0.340}{6.4} = 0.053$$

Referring to Fig. 4, the oxygen concentration is 3.5 parts per million.

Calibration curves

Connect the apparatus to a source of purified helium gas. Open stop-cock 5 and bring the level of the sulfuric acid solution to level E. Close stop-cock 5. Follow the steps as outlined for analysis of sample gas up to the point where the sample gas would be admitted to the system. At this point the homogeneous analytical solution has been brought to level D and the prepared analytical solution is isolated by stop-cocks 3 and 4. With

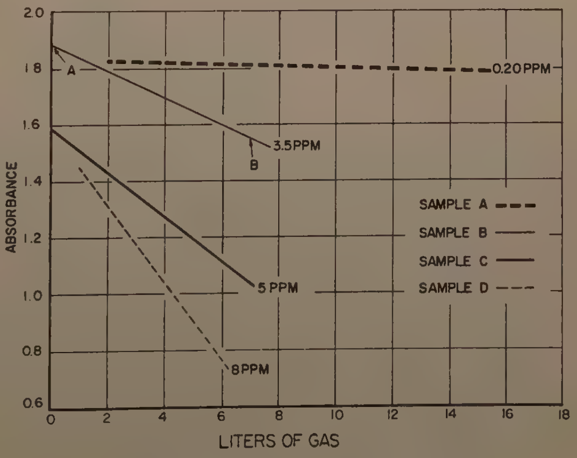

Fig. 5. Typical analytical plots.

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stop-cock 1 open only to the source of purified gas, adjust the rate of flow to 100 ml per minute.

As simultaneously as is possible, throw the switch to the power-supply for the electrolytic cell, adjust the current to six milliamperes, start a stop-watch, and read the absorbance. Record absorbance at exactly 1- or 2-minute intervals. Maintain a watch on the milliammeter to secure a constant current flow of six milliamperes. Record the volume of the carrier-gas at the same time that the absorbance reading is taken. Continue readings until the decrease in absorbance levels off, approximately at 0.6 to 0.5.

Plot the absorbance as ordinate and the volume of carrier-gas as abscissa as shown in Fig. 6, Line 1. Fig. 6, Line 2, is the pre-determined blank of the carrier gas. Calculate the corrected absorbance at each point by subtracting the absorbance of the blank, line 2, from the observed absorbance, line 1.

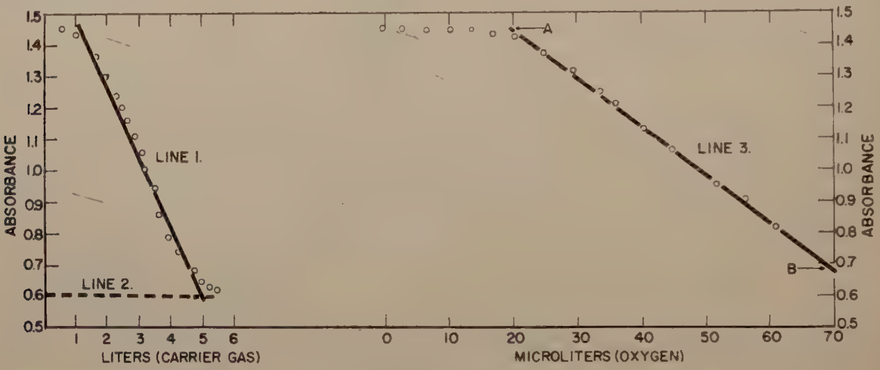

Fig. 6. Typical calibration run.

Calculate the amount of oxygen generated at a given time-interval by the following equation:

$$\text{Oxygen, in microliters} = 0.01615\, I\, t\, \frac{T}{P} \; \ldots\ldots \text{Eq. 2}$$

Where I = the current in milliamperes which is passed through the electrolytic cell
t = the time in seconds the current flows
T = the absolute temperature during the analysis
P = the barometric pressure in millimeters.

Plot the corrected absorbance as ordinate and the oxygen generated (microliters) as the abscissa, Line 3. Calculate the calibration factor, F, from Line 3 as follows:

$$F = \frac{\Delta A^1}{\Delta V^1} \; \ldots\ldots \text{Eq. 3}$$

Where ΔA^1 = change in corrected absorbance between points A and B
ΔV^1 = the difference in microliters between points A and B

For example, the factor is calculated from the calibration curve in Fig. 6 in the following manner.

$$F = \frac{1.452 - 0.682}{70 - 20} = 0.015 \text{ (absorbance per microliter)}$$

Set up two calibration plots as follows. One should cover the range from 1 to 15 parts per million (Fig. 4). The other should cover the range from 0 to 1 part per million (Fig. 4). The oxygen in parts per million times the factor F is equal to the corrected tangent of the analytical plot.

$$\text{"Analytical Tangent"} = F \times O_2\text{, ppm.} \; \ldots\ldots \text{Eq. 4}$$

Plot "oxygen, parts per million" *versus* "analytical tangent".

EXPERIMENTAL RESULTS

Pumping mechanism and efficiency of oxygen absorption

The apparatus was first set up as specified by BRADY[7], Fig. 2B, except that ball and socket joints were substituted for tygon joints to prevent oxygen diffusion. The pumping mechanism did not work as efficiently as expected. At the liquid-gas contact point, (Fig. 2B), where the sample gas forces the analytical reagent up through the gas scrubber, only a portion of the liquid went over the top while the majority of the liquid fell back to the liquid-gas contact point. This meant poor circulation of liquid for a given volume of gas throughput. The effects of the poor pumping efficiency could be observed visually; the color of the analytical solution became much lighter at the liquid gas contact point than it was in the gas-separator. Moreover the rate of gas-flow was highly critical.

After testing several experimental models, the dimensions given in Fig. 2A were selected. Decreasing the diameter of the bore made the gas pressure more effective in lifting all the liquid over the top. Extension of the 4-mm tube below the liquid-gas contact point meant that a greater volume of liquid was lifted for each pumping stroke.

In this model the gas forces the liquid all the way through the gas-scrubber. There is no drop-back of the analytical solution. The liquid is darker at the liquid-gas contact point than it is in the gas-separator. The flow-rate can be varied without changing the calibration factor markedly.

The greater efficiency of oxygen absorption in our modification is shown (Fig. 7) by plotting the slopes of the analytical plots, such as those shown in Fig. 4, against the parts per million oxygen of the sample gas. Fig. 7, Line 1, is calculated from our calibrations and from actual gas samples. The oxygen content of these gas samples was verified by analysis by the WINKLER method[6]. Fig. 7, Line 2, is calculated from calibration data published by BRADY[7]. Fig. 7, Line 3, is calculated from data obtained by MANN[8] using an unmodified BRADY apparatus. That our system is much more efficient can be plainly seen, since the slope of the line of a given concentration of oxygen is more than twice as great by our modification than it is by the BRADY method.

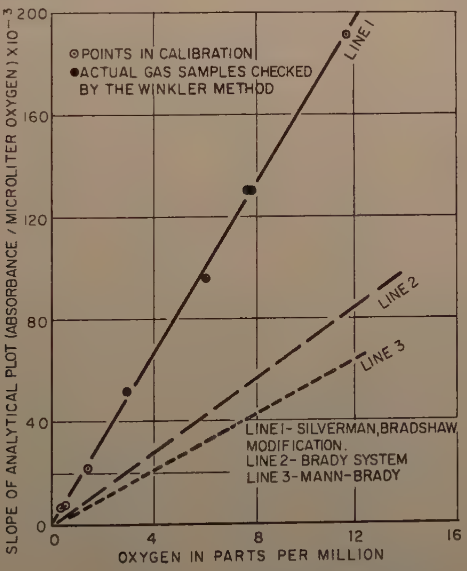

Fig. 7. Efficiency of various BRADY systems.

Preparation of carrier-free gas

In early work the preliminary purification of helium, which averages 5 parts per million oxygen, and the purification of hydrogen, which averages 2.5 parts per million oxygen was studied, until a carrier-gas containing less than 0.5 parts per million oxygen was available.

The experimental de-oxygenation of helium and of hydrogen was first attempted using sodium anthraquinone-beta-sulfonate scrubbing solution, purifying grade. 130 g of amalgamated zinc shot plus 200 ml of scrubbing solution was optimum for each wash bottle. The results obtained in hydrogen and helium purification are shown in Table I. The lowest and most dependable results were obtained when hydrogen was put through a series of three gas-washing bottles. This type of scrubbing solution is soon exhausted and should be changed after two-weeks of exposure.

TABLE I

PURIFICATION OF CARRIER GAS USING SODIUM ANTHRAQUINONE-BETA-SULFONATE SCRUBBING SOLUTION

Gas used	*Number of gas washing bottles*	*Oxygen-concentration in parts per million*	
		Before treatment	*After treatment*
Hydrogen	3	2.5	0.1 0.1 0.3 0.3 0.4
Hydrogen	2	2.5	0.6 0.9 1.25
Hydrogen	1	2.5	1.3
Helium	3	5	0.5 0.8 1.4
Helium	4	5	1.4

In the second attempt a system of NaK bubblers produced a purer carrier gas containing 0.1 part per million or less of oxygen. The results were reproducible. The NaK bubbler, specified under reagents, can be used for helium purification until exhausted ($3.5 \cdot 10^4$ cu ft of helium). The after-treatment oxygen-concentration should remain less than 0.1 part per million oxygen.

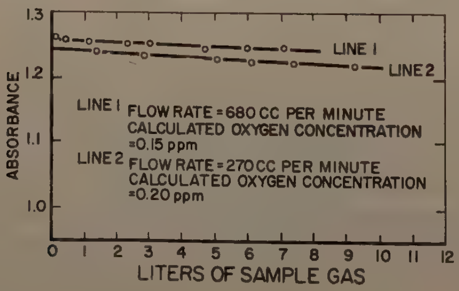

Fig. 8. Effect of flow rate on analysis.

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Effect of flow-rate

The flow-rate was varied from 100 to 300 ml per minute. Such variation did not significantly affect the calibration factor or the oxygen determination. However, a slow pumping speed (100 ml per min) is preferred when the oxygen concentration is greater than one part per million, in order to obtain a smooth analytical plot.

When the oxygen concentration is less than one part per million the flow-rate can be increased to 300 ml per minute without significantly affecting the analysis. Increasing the flow-rate to approximately 700 ml per minute affects the analysis as shown by the analytical plots in Fig. 8; changing the flow-rate from 270 ml to 700 ml per minute decreased the observed concentration from 0.20 to 0.15 parts per million.

Absorbance measurements

A Klett instrument was used in the first trials. While this instrument is sensitive enough for use when the oxygen concentration is greater than one part per million, it cannot be used for lower oxygen concentrations. In order to obtain the precision and accuracy described in this paper a Beckman, model DU, spectrophotometer was used. The absorption curve is shown in Fig. 9. For our work a wave-length of 530 mμ, and a slit-width of 0.04 was selected.

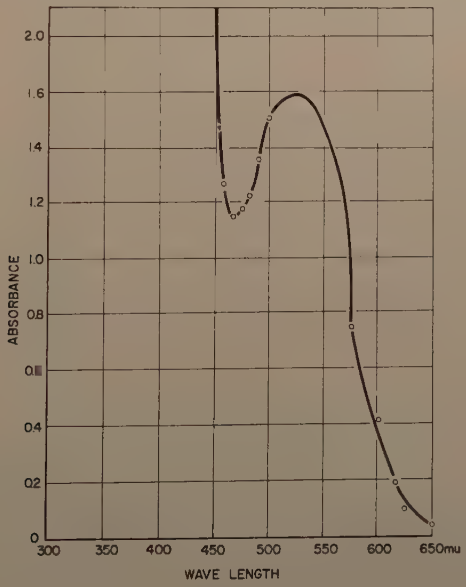

Fig. 9. Spectrophotometric curve of reduced sodium anthraquinone-beta-sulfonate.

Precision, accuracy and range of the method

The precision of the method was tested in a series of experiments using various gas samples for duplicate analyses, Table II. The standard deviation ranges from ± 0.004 part per million oxygen when the oxygen content is 0.01 part per million to ± 0.2 part per million oxygen when the oxygen content is 5 parts per million.

TABLE II

REPRODUCIBILITY OF ANALYSIS

Sample	*Oxygen in parts per million by volume*		*Standard deviation*	*Error %*
	Individual analyses	*Average*		
1	0.016 0.011	0.013	±0.004	28
2	0.023 0.017	0.020	±0.004	21
3	0.027 0.051	0.039	±0.017	44
4	0.050 0.035	0.042	±0.011	26
5*	0.103 0.113	0.108	±0.007	6.5
6	0.15 0.10	0.13	±0.04	28
7	0.26 0.28	0.27	±0.01	5
8	0.26 0.31	0.28	±0.04	13
9	0.41 0.44	0.43	±0.02	5
10*	0.60 0.70	0.65	±0.07	11
11	2.89 2.89	2.89	0.0	0
12	6.89 6.98	6.94	±0.06	1
13*	8.75 9.04	8.90	±0.21	2.3

* Samples were done on different days or at different times.

The percent error varies from 30 to 40 percent in the low range of oxygen concentration (0.01 to 0.10 part per million) through 5 to 13 percent in the median range (0.1 to 1 part per million oxygen) to 0 to 2 percent in the upper range (1 to 15 parts per million oxygen). The precision is not affected when the determinations are carried out on different days.

The accuracy of the method was checked by comparative analyses of various gas samples by the method described herein and a modified WINKLER method[6], Table III. The analyses by the two different methods do not differ from each other significantly. The two methods are calibrated by different means. The modified Brady method is calibrated by electrolytically generated oxygen, and the modified WINKLER method is calibrated by the oxidative properties of potassium dichromate. It is unlikely that

TABLE III

COMPARISON OF BRADY AND WINKLER METHODS

Sample gas	*Oxygen in parts per million by volume*			
	Brady Method (modified)		*Winkler Method*	
	Individual analysis	*Average analysis*	*Individual analysis*	*Average analysis*
Helium	6.9 7.0	6.9	6.5 6.8	6.7
Hydrogen	2.9 2.9	2.9	2.9 3.0	2.9
Purified* Hydrogen	0.4 0.0 0.0 0.3 0.3	0.2	0	

* This was purified using gas-scrubbers containing sodium-anthroquinone-beta-sulfonate, and the samples may not have been uniform.

two such widely divergent methods could exhibit the same error; therefore both methods should be accurate.

The range of the method described here-in is 0.01 to 15 parts per million oxygen. The method has been used successfully to analyse hydrogen, nitrogen, helium and argon.

DISCUSSION

A rapid, precise and accurate method is described for the analysis of micro-amounts of oxygen in hydrogen, nitrogen and inert gases. The method, a modification of that of BRADY, has a range of 0.01 to 15 parts per million oxygen.

Greater sensitivity to small amounts of oxygen is obtained by a more efficient pumping system and the use of a more sensitive photometric instrument to measure absorbance. The method is unique in being usable to measure oxygen concentrations as low as 0.01 to 0.10 part per million oxygen. The lowest concentration of oxygen detectible is 0.005 parts per million oxygen. BRADY reported a range of 1 to 100 parts per million oxygen.

The method is a dynamic one, requiring 5 to 20 liters of sample gas. However, static methods, analysing one liter of gas or less, cannot detect much less than 0.5 part per million oxygen according to PEPKOWITZ[5] and SILVERMAN AND BRADSHAW[6]. Greater reproducibility is obtained by determining the oxygen concentration from the slope of the rate of change of absorbance rather than from the difference in absorbance (BRADY's method). A double set of graphs is used to obtain the final oxygen result.

The standard deviation of the method is ± 0.004 to ± 0.04 in the low range of oxygen concentration (0.01 to 0.10 part per million oxygen), ± 0.01 to ± 0.07 in the medium range of oxygen concentration (0.1 to 1.0 part per million oxygen) and ± 0.0 to ± 0.2 in the upper range of oxygen concentration (1 to 15 parts per million oxygen). Such precision has not been attained in either dynamic or static test methods previously published. BRADY reported a precision of 5 parts per million when the oxygen concentration is 50 parts per million. PEPKOWITZ[5] reported a standard deviation of ± 0.8 part per million and SILVERMAN AND BRADSHAW[6] a standard deviation of ± 0.3 part per million when the oxygen concentration is 1 to 30 parts per million using the static WINKLER method.

The preparation of the reduced analytical solution for the modified BRADY procedure is accomplished by direct mixing rather than by BRADY's routine of premixing with purified carrier gas. This is desirable because our higher efficiency system is more sensitive to small amounts of oxygen than is that of BRADY. Even carrier-gas containing 0.1 part per million oxygen has a noticeable blank in our improved apparatus. This use of direct mixing shortens the preparation time from 15 minutes (BRADY) to 5 minutes and makes possible a more rapid determination.

The modified method is rapid, requiring one hour or less to complete an analysis. The same analysis by the BRADY method would take approximately three times as long in the lower ranges of oxygen concentration. Static (WINKLER) methods require at least four hours.

An improved source of oxygen-free gas containing 0.1 part per million oxygen or less is requisite to the greater precision and accuracy described.

This report is based on studies conducted for the Atomic Energy Commission under contract AT-11-1-GEN-8.

SUMMARY

The modified BRADY method is a rapid one, requiring only about one hour for the analysis, but requires large samples of gas, 5 to 20 liters. The precision of the method described here-in is ±0.004 to ±0.4 in the low range of oxygen-concentration (0.01 to 0.10 part per million oxygen), ± 0.01 to ± 0.07 in the medium range of oxygen-concentration (0.1 to 1.0 part per million oxygen) and ± 0.0 to ± 0.2 in the upper range of oxygen-concentration (1 to 15 parts per million oxygen). The best precision (WINKLER method) previously reported was ± 0.3 part per million oxygen. The range of the method is 0.01 to 15 parts per million oxygen. The minimum amount of oxygen detectible is 0.005 part per million.

RÉSUMÉ

Cette méthode de BRADY modifiée est rapide. Une analyse ne dure qu'environ une heure, mais elle nécessite de grands volumes de gaz à analyser, 5 à 20 litres. La précision de la méthode décrite ici est: de ± 0.004 à ± 0.4 pour de faibles concentrations en oxygène (0.01 à 0.1 p.p.m.), de ± 0.01 à ± 0.07 pour des concentrations moyennes en oxygène (0.1 à 1.0 p.p.m.) et de ± 0.0 à ± 0.2 pour les concentrations les plus fortes (1 à 15 p.p.m. d'oxygène). La meilleure précision jusqu'ici signalée (méthode de WINKLER) était de ± 0.3 p.p.m. d'oxygène. Le procédé décrit permet de doser des concentrations en oxygène de 0.01 à 15 p.p.m. La quantité minimum d'oxygène décelable est de 0.005 p.p.m.

ZUSAMMENFASSUNG

Die hier beschriebene Modifikation der BRADY'schen Methode is rasch, denn für eine Analyse genügt eine Stunde, sie erfordert aber grosse Gasproben (5 bis 20 Liter). Die Genauigkeit dieser Methode beträgt ± 0.004 bis ± 0.4 für niedrige Sauerstoffkonzentrationen (± 0.01 bis 0.1 p.p.m.), ± 0.01 bis ± 0.07 für mittlere Sauerstoffkonzentrationen (0.1 bis 1 p.p.m.) und ± 0.0 bis ± 0.2 für die höchsten Konzentrationen (1-15 p.p.m. Sauerstoff). Die bis heute beste Präzision wurde für die WINKLER'sche Methode aufgeführt und betrug ±0.3 p.p.m. Sauerstoff. Die beschriebene Methode erlaubt Sauerstoffkonzentrationen von 0.01-15 p.p.m. zu bestimmen. Die kleinste, bestimmbare Menge Sauerstoff beträgt 0.005 p.p.m.

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SÉPARATION Rb-Cs PAR CHROMATOGRAPHIE SUR CELLULOSE EXTRACTION SÉLECTIVE DU ^{137}Cs DE FISSION

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INTRODUCTION

Dans le cadre du programme de recherches sur la séparation des produits de fission de l'uranium, nous avons recherché, d'une part, une méthode microchimique de séparation chromatographique Rb-Cs sur cellulose et d'autre part, une méthode d'extraction aussi rapide que possible du césium de fission, ,,carrier free''.

Ces deux éléments sont d'importants produits de fission et tout spécialement $_{137}$Cs (33 ans) offre des perspectives d'applications industrielles intéressantes[1,2].

Le problème de la séparation chromatographique Rb–Cs a été abordé déjà par d'autres auteurs[3,4,5] qui se plaçaient, sauf en ce qui concerne LEDERER, du point de vue de la simple séparation et de l'identification des alcalins entr'eux.

Dans cette étude, nous nous sommes limités à la méthode de séparation chromatographique sur cellulose.

PRODUITS — MESURES

a. *Papiers*: Pour les essais sur bandes de papier, nous avons utilisé le Whatman no. 1; les bandes ont 1 cm de large et environ 20 cm de longueur utile.
Les expériences sur colonne ont été effectuées au moyen de poudre de cellulose Whatman grade B, purifiée suivant le procédé décrit dans une publication antérieure[6].

b. *Radioisotopes*: Nous disposions pour la mise au point et l'application des procédés préconisés des produits suivants:
   1. ^{86}RbCl (19.5 j.), en provenance de Harwell, produit par activation neutronique.
   2. ^{137}Cs (33 a.) de fission, en provenance de Harwell; il contient également un peu de ^{134}Cs (2.3 a.).
   3. ^{134}Cs (2.3 a.) extrait du RbCl activé à la pile de Harwell (impureté).
   4. U irradié à la pile de Harwell durant un mois; nous disposions de deux échantillons: le premier a été utilisé six mois après l'irradiation (Uranium A); le second seulement quarante jours après la fin de l'irradiation (Uranium B).
   Nous nous plaisons à remercier M. H. HUBERT, directeur au centre des applications de l'énergie nucléaire, qui a eu l'amabilité de mettre ces échantillons à notre disposition.

c. *Mesures*: La détection sur bande de papier a été faite généralement par mesure d'activité au compteur G.M.; dans certains cas, cependant, nous avons été obligés d'utiliser la détection chimique au cobaltinitrite de sodium.
Pour les essais sur colonne, les différentes fractions recueillies au moyen d'un appareil automatique sont généralement évaporées en cuvette et les concentrations sont déterminées par

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mesure de l'activité du résidu. Dans certains cas, nous avons dosé le rubidium par spectrophotométrie de flamme, après dilution par 3 à 4 volumes de méthanol (λ = 7800 Å). Enfin, dans un cas, nous avons simplement déterminé le pic du rubidium par pesée du résidu d'évaporation de RbCl; il s'agissait d'une expérience d'extraction du césium d'un échantillon de RbCl irradié à la pile.

ESSAIS DE SÉPARATION CHROMATOGRAPHIQUE Rb-Cs

1. Élution au mélange méthanol-HCl 12N

Nous avons commencé par essayer l'élution chromatographique au moyen de mélange méthanol-HCl 12*N* qui s'est avéré très efficace pour la séparation des alcalino-terreux et satisfaisante pour celle de Li, Na, K.

Ces essais ont été faits sur une colonne de cellulose de 9 mm de diamètre intérieur et de 20 cm de haut, à la température constante de 18° C. Nous avons essayé des éluants contenant, pour 100 volumes de méthanol, 0 à 5 volumes de HCl 12*N*. Les résultats sont donnés dans la Fig. 1; elle situe le début, le maximum et la fin (caractérisée par le dixième du maximum) des pics du rubidium et du césium. On peut voir que la séparation est pratiquement nulle dans tout le domaine exploré.

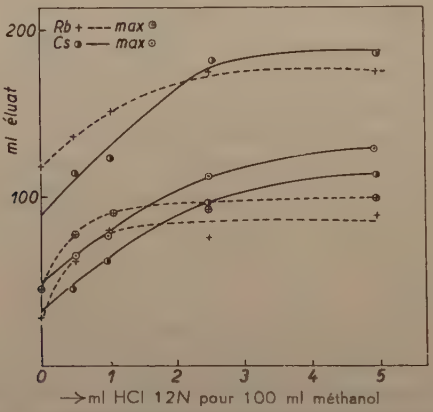

Fig. 1. Essais de séparation chromatographique sur colonne de cellulose au moyen d'éluants à base de méthanol et de HCl 12*N*.

Nous n'avons pas jugé utile de poursuivre ces essais avec des éluants plus riches en acide chlorhydrique d'autant plus qu'avec des mélanges contenant du méthanol et de l'acide chlorhydrique en parts à peu près égales, on observe une inversion dans l'ordre des élutions: le césium migre plus rapidement que le rubidium et le potassium[3].

D'autre part une trop forte concentration en acide chlorhydrique désagrège assez rapidement la cellulose.

2. Recherche d'un nouvel éluant

Nous avons procédé à des essais d'orientation sur bandes de papier avec différents solvants; les quantités de Rb et Cs mises en oeuvre dans chaque essai étaient de l'ordre de 100 à 200 γ et la révélation se faisait au cobaltinitrite.

Les Tableaux I et II résument les résultats obtenus:

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TABLEAU I

ÉLUANTS A BASE DE MÉTHANOL

Éluant	*Volumes* A	*Volumes* B	*Volumes* C	R_F *de* Rb^+	R_F *de* Cs^+	$p = \frac{R_F Cs}{R_F Rb}$
Méthanol pur				0.26	0.25	1
Méthanol (A)	100	1	5	0.14	0.17	
HCl 12*N* (B)			10	0.22	0.18	
H_2O (C)			20	0.38	0.36	1
			50	0.55	0.55	
			100	0.65	0.65	
	100	0.1	10	0.33	0.33	1
			20	0.43	0.43	
Méthanol (A)	100	1		0.2	0.2	1
HNO_3(conc.) (B)		0.1		0.2	0.2	
Méthanol (A)	100	1		0.12	0.12	1
$HClO_4$(conc.) (B)		0.1		0.2	0.2	
Méthanol (A)	100	1		0.23	0.23	1
Acide acétique		0.1		0.22	0.25	
glacial (B)						
Méthanol (A)	100	(10 g)		0.32	0.30	1
Acide monochloracétique (B						
Méthanol (A)	100	(saturé)		0.2	0.2	1
NH_4Cl (B)						
Méthanol (A)	100	2		0.2	0.2	1
NH_4OH aq. (B)	$CsNO_3$			0.29	0.26	
	$RbNO_3$					
Méthanol (A)	100	(10 g)		0.28	0.28	1
Phénol (B)						

TABLEAU II

ÉLUANTS DIVERS

Éluant	*Volumes* A	*Volumes* B	R_F *de* Rb^+	R_F *de* Cs^+	$p = \frac{R_F Cs}{R_F Rb}$
Pyridine pure			0.07	0.07	1
Pyridine (A)	100	20	0.15	0.15	1
H_2O (B)					
Morpholine (A)	100	0	0	0	1
H_2O (B)		15	0.25	0.25	
Acétylacétone	équilibrée avec HCl 6*N*		0	0	
Phénol	équilibré avec HCl aq. 20 % (v/v)		0.31	0.56	**1.8**
Acétone (A)	100	5	0.07	0.07	1
HNO_3 conc. (B)					

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On constate que seul l'éluant à base de phénol, déjà proposé par STEEL[4] et utilisé par LEDERER[5] donne une différence de R_F suffisante et des taches bien localisées.

Nous avons ensuite voulu nous rendre compte si le phénol équilibré avec HCl $2N$ pouvait également convenir pour une séparation sur colonne; ces essais ont été effectués au moyen d'une colonne thermostatisée à 18° C, de 1 cm de diamètre et contenant une hauteur de cellulose de 8 cm (2.5 g de cellulose); par essai, la quantité de RbCl utilisée était d'environ 10 mg et celle de CsCl beaucoup plus faible ($< 50\ \gamma$).

La Fig. 2b reproduit l'une des courbes d'élution obtenue dans une série de quatre essais consécutifs destinés à éprouver la reproductibilité de la méthode; les quatre chromatogrammes étaient superposables.

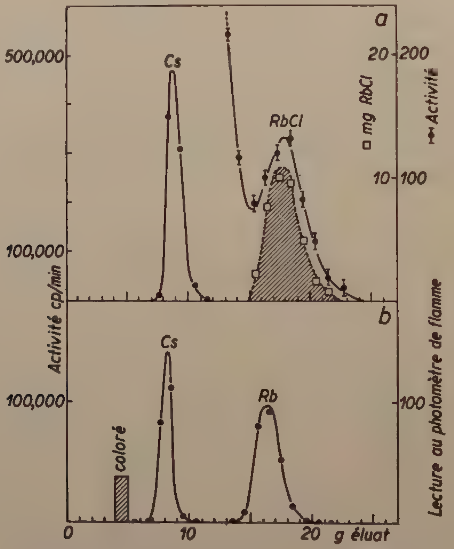

Fig. 2a et 2b. Séparations chromatographiques Rb-Cs sur colonne de cellulose par élution au moyen de phénol équilibré avec HCl $2N$.

Notons que le pic du césium a été déterminé par mesure d'activité (^{134}Cs) tandis que celui du rubidium a été relevé au spectrophotomètre de flamme. La séparation sur colonne est excellente: l'activité de la cuvette située deux places avant celle où l'on commence à détecter le rubidium, représente $\frac{2}{10.000}$ de l'activité totale du césium.

Le volume libre de la colonne est de l'ordre de 4 g d'éluant; on peut l'apprécier grâce à la coloration brunâtre du petit volume de phénol qui a servi à amener les produits sur la colonne; ce volume était de 0.5 ml et il se retrouve dans la 5e fraction.

3. *Application*

Nous avons eu l'occasion de vérifier l'intérêt de cette méthode en radiochimie; nous disposions de RbCl irradié à Harwell (^{86}Rb: 19.5 j.), qui après décroissance presque complète du rubidium, gardait une activité parasite très importante; nous l'avons soumis à une chromatographie, à la fois sur bande de papier et sur colonne.

Après une mise en équilibre de la colonne avec le phénol équilibré avec HCl $2N$, nous y avons versé 1 ml d'une solution saturée du RbCl impur dans l'éluant (∿ 40 mg de RbCl): la Fig. 2a montre le chromatogramme obtenu: un pic intense à la place du césium (environ 750.000 cps/min): les mesures d'absorption et de décroissance cadrent également avec cette attribution; le chlorure de rubidium utilisé pour l'irradiation contenait des traces de césium qui ont été également activées en donnant du ^{134}Cs (2.3 a.). Cette même remarque a été faite récemment par d'autres auteurs[7].

Les fractions d'élution contenant normalement le chlorure de rubidium ont été recueillies dans des cuvettes en verre; après évaporation de l'éluant, le résidu a été pesé (voir la courbe d'élution en hachuré; il est d'ailleurs à noter que ce rubidium possède encore une très faible activité dont la courbe concorde bien avec celle déterminée par gravimétrie).

On voit ainsi que le procédé chromatographique sur colonne est intéressant non seulement du point de vue analytique mais également d'un point de vue préparatif: il peut convenir parfaitement pour préparer du chlorure de rubidium exempt de césium destiné à une irradiation ou si l'on veut, pour purifier le chlorure de rubidium activé: la chose est d'autant plus intéressante que la période du ^{86}Rb est relativement courte vis-à-vis de celle du césium d'activation.

Si l'on désire contrôler rapidement la pureté radiochimique d'un échantillon de RbCl d'activation, un chromatogramme sur bande de papier est tout indiqué.

La Fig. 3 montre le résultat obtenu avec le même échantillon de RbCl: *a* est un témoin obtenu avec 100 γ de CsCl marqué avec ^{137}Cs; *b* est le chromatogramme du RbCl de Harwell quelques mois après l'irradiation: l'essai d'activité montre à nouveau l'existence du césium: la position du rubidium a été déterminée au cobaltinitrite et vérifiée par mesure d'activité (voir *c*).

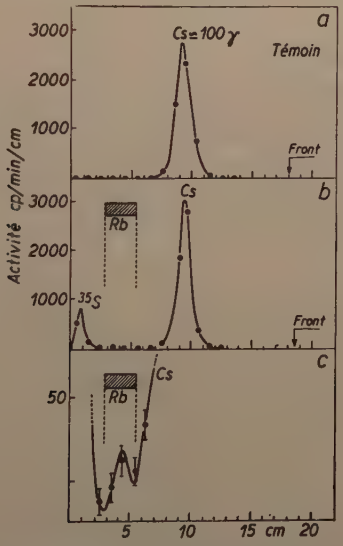

Fig. 3. Chromatogramme sur bande de papier de RbCl irradié à Harwell. Élution au phénol équilibré avec HCl 2*N*.

Il est intéressant de constater qu'il existe encore une certaine activité près de l'origine: il s'agit d'un radioélément d'une période de l'ordre de 90 jours et de très faible énergie (E_{max} = 0.14 à 0.17 Mev.); il s'agit vraisemblablement de ^{35}S (87.1 j.; E_{max} = 0.167 Mev.) produit par une réaction (n,p) sur le ^{35}Cl de RbCl[8].

EXTRACTION DU ^{137}Cs DE FISSION

Le césium est un des produits de fission de longue période et une méthode d'extraction de ce produit à l'état ,,carrier free'', par un procédé simple, serait intéressante.

Quelques essais préliminaires nous ont rapidement montré que le phénol équilibré avec HCl 2*N* semble parfaitement convenir: Sr^{+2}, Ba^{+2}, Ce^{+3}, terres rares, Pb^{+2}, Pd^{+2}, Sn^{+2} ne s'éluent pratiquement pas; au contraire pour I^- et Sb^{+3}, on obtient des R_F respectivement de 0.1 et 0.35. I et IO_3^- (réduit au contact de l'éluant) migrent avec un R_F voisin de l'unité; cet ,,iode'' n'est plus extractible par CCl_4.

Signalons que dans l'uranium irradié durant un mois à la pile, on retrouve, six mois après la fin de l'irradiation, principalement les émetteurs β suivants avec leurs contributions approximatives au rayonnement[9] suivantes:

$$^{144}\text{Ce}\ (^{144}\text{Pr}): 40\%;\ ^{91}\text{Y}: 20\%;\ ^{90}\text{Sr}\ (^{90}\text{Y}): 20\%;\ ^{95}\text{Zr}\ (^{95}\text{Nb}): 10\%;$$
$$^{103}\text{Ru-}^{106}\text{Ru}\ (^{106}\text{Rh}): 4\%;\ ^{137}\text{Cs}: 2\%;\ \text{Te}: 1\%.$$

Ceci nous a amené à essayer immédiatement un chromatogramme sur la solution nitrique d'uranium irradié (Uranium A).

1. *Essais sur bandes de papier*

a) *Éluant: phénol équilibré avec HCl 2N*

Lors du premier essai (Fig. 4c), nous avons été surpris de constater la présence d'une activité relativement importante de R_F voisin de 1; elle est accompagnée d'une intense coloration brune formée à l'origine, quand le phénol entre en contact avec la tache de départ.

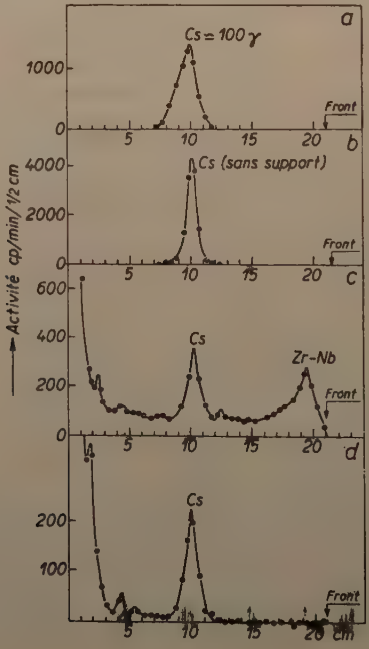

Fig. 4. Chromatogramme sur bande de papier d'uranium irradié à la pile. Élution au phénol équilibré avec HCl 2*N* (six mois après la fin de l'irradiation).

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Cette activité parasite semble avoir laissé une traînée plus ou moins constante tout au long du chromatogramme et l'activité β représente environ 10% de l'activité totale des produits de fission restant à l'origine; cela nous fit supposer que nous étions en présence de ^{95}Zr (colloïdal?). Des essais ultérieurs ont confirmé cette attribution.

La plus grosse partie de l'activité β (Ce, Y, Sr) reste à l'origine: on observe néanmoins un léger pic qui se situe vers $R_F = 0.1$. Nous avons trouvé qu'il s'agissait du ruthénium: ^{103}Ru et ^{106}Ru (+ ^{106}Rh de filiation).

Enfin, au milieu du chromatogramme, on observe le pic de ^{137}Cs qui se détache nettement sur le fond continu; la concordance avec un échantillon de ^{137}Cs ,,carrier free'' élué simultanément est frappante (Fig. 4b). Lorsqu'on y ajoute 100 γ d'entraîneur inactif, le pic devient un peu plus large (Fig. 4a).

Nous avons réussi à nous débarrasser de l'action gênante du zirconium, soit en déposant sur la bande de papier une goutte d'eau oxygénée (à 30 volumes) à l'endroit où sera mise la solution ($\sim 3 \mu l$) contenant l'uranium et les produits de fission, soit en exposant le papier après chargement de la solution à séparer à des vapeurs de sulfure d'ammonium.

La Fig. 4d montre le résultat obtenu par traitement avec H_2O_2.

b) Éluant: phénol équilibré avec H_2O

Les résultats sont très similaires (Fig. 5): le R_F de Cs^+ n'a pratiquement pas varié mais le pic est un peu plus large. Près de l'origine, le pic de Ru se détache mieux ($R_F = 0.14$).

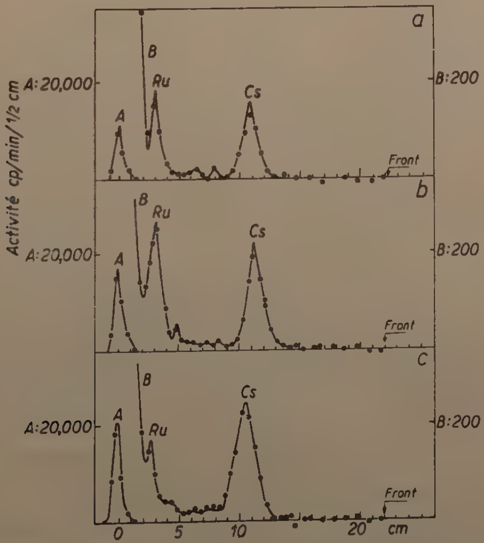

Fig. 5. Chromatogramme sur bande de papier d'uranium irradié à la pile. Élution au moyen de phénol équilibré avec l'eau (six mois après la fin de l'irradiation).
a) Phénol éq. H_2O; bande traitée par H_2O_2.
b) Phénol éq. H_2O.
c) Phénol éq. H_2O; origine traitée par $(NH_4)_2S$.

Dans ce cas, même sans traitement du papier [H_2O_2 ou vapeur de $(NH_4)_2S$], nous n'avons plus observé de radioélément s'éluant plus vite que le césium.

Dans l'ensemble des essais effectués sur bandes de papier, nous avons constaté que l'activité du pic de Cs^+ représente en moyenne 2.2% de l'activité totale, valeur en accord avec les données de la littérature.

On voit ainsi qu'au moyen du phénol équilibré avec HCl 2*N* ou H_2O, il est possible d'éluer sélectivement le césium de la solution d'attaque de l'uranium contenant tous les produits de fission. Cette méthode est extrêmement rapide et fournit un produit très pur.

Nous avons encore voulu nous rendre compte si le procédé reste aussi sélectif lorsqu'on part d'uranium fraîchement retiré de la pile; à cet effet, nous avons utilisé l'uranium B (voir p. 527). L'essai a été fait sur bande de papier traitée au préalable avec H_2O_2.

Un des chromatogrammes obtenus est représenté dans la Fig. 6. Par suite de l'activité élevée de cet uranium, nous avons été obligés de découper l'origine de la bande où était concentrée la majeure partie des radioéléments de fission, pour pouvoir obtenir des mesures correctes des activités relativement faibles réparties le long du chromatogramme (Fig. 6b). On observe néanmoins, en plus du pic de ^{137}Cs (comparé au témoin de la Fig. 6a) un pic supplémentaire au front de l'éluant.

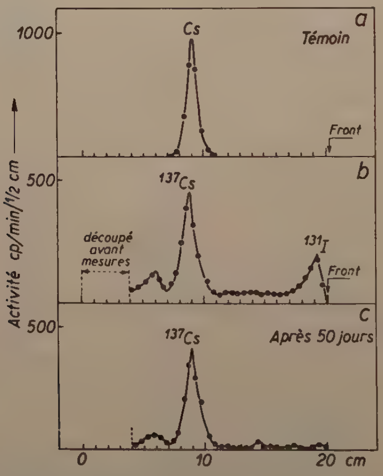

Fig. 6. Chromatogrammes sur bandes de papier d'uranium irradié à la pile. Élution au moyen de phénol équilibré avec HCl 2*N* (quarante jours après la fin de l'irradiation).

Les mesures de décroissance et d'absorption nous ont montré qu'il s'agit en majeure partie de ^{131}I (période 8 j.; $E_{max} = 0.6$ Mev.). Sur la Fig. 6c se trouve le même chromatogramme mesuré 50 jours plus tard, après la décroissance presque complète de ^{131}I.

Le petit pic situé à gauche de celui de Cs^+ (Fig. 6b et 6c) n'a pas encore été identifié; il se pourrait que ce soit ^{125}Sb, puisque nous avons trouvé que son R_F est de l'ordre de 0.35.

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2. *Essai sur colonne de poudre de cellulose*

L'expérience a été faite sur une colonne de 8 cm de longueur et de 1 cm de diamètre. La température est maintenue constante à 18° C; l'élution se fait au moyen de phénol équilibré avec HCl $2N$.

Après la mise en régime de la colonne avec l'éluant, on y introduit une petite goutte de la solution nitrique d'uranium irradié (uranium A) et l'on commence l'élution.

Sur le chromatogramme de la Fig. 7a, on remarque la présence d'une importante activité juste après la sortie du premier volume libre, en même temps que la coloration brune intense formée au départ au contact de la solution nitrique.

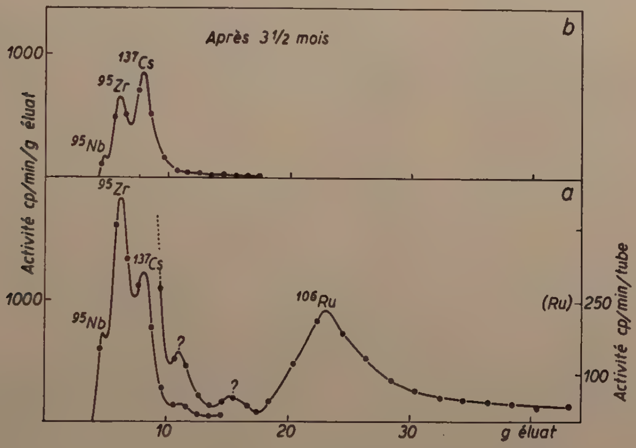

Fig. 7. Chromatogramme sur colonne de cellulose de l'uranium irradié à la pile (six mois après la fin de l'irradiation). Élution au phénol équilibré avec HCl $2N$.

Cette activité ne pouvait manifestement pas être due uniquement au ^{137}Cs dont le maximum se situe vers deux volumes libres.

L'examen des décroissances des portions initiales, ainsi que des mesures d'absorption nous ont conduit aux attributions suivantes:

le premier pic est dû surtout à ^{95}Nb (35 j.),
le deuxième à ^{95}Zr (65 j.),
le troisième à ^{137}Cs à la place attendue (Fig. 7b.).

Cette dernière figure nous montre la répartition des activités (Ru excepté) $3^1/_2$ mois plus tard.

Un dernier pic étalé, a été attribué au ^{106}Ru + ^{106}Rh (et évidemment ce qui reste de ^{143}Ru), en effet:

i. C'est le seul radioélément qui, parmi les produits de fission susceptibles de se trouver en quantité notable à ce moment, ait une énergie de rayonnement β aussi élevée: 3.5 à 3.9 Mev. (due au ^{106}Rh, filiation de ^{106}Ru, de période 30 s.).

ii. D'autre part, une fraction notable (> 30%) de l'activité a pu être distillée ,,carrier free'' après oxidation par KBrO$_3$. Les portions non distillées ont pratiquement la même énergie de rayonnement.

iii. Enfin la période trouvée est de l'ordre de l'année (^{106}Ru, période: 1 a.).

Si, avant de mettre les produits sur la colonne, on y laisse tomber quelques gouttes d'eau oxygénée à 30 volumes, on observe de nouveau, comme sur bande de papier, le pic très net du ^{137}Cs, suivi de celui du ruthénium (Fig. 8). On observe néanmoins, avant le pic du césium, une très petite activité qui n'a pas été identifiée; il ne s'agit certainement pas d'une anomalie dans le pic de ^{137}Cs car nous avons observé une décroissance nette après deux mois.

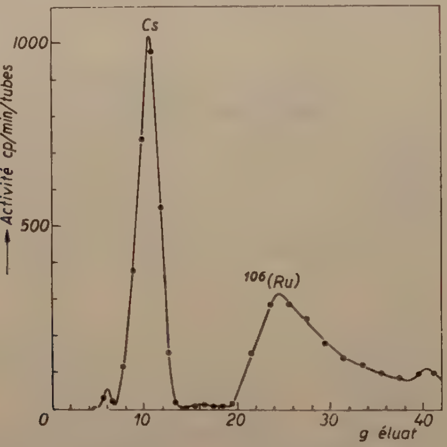

Fig. 8. Même essai que dans la Fig. 7. Traitement avec une goutte d'eau oxygénée.

REMERCIEMENTS

L'un de nous (J. F.) se plaît à remercier Messieurs les professeurs G. GUEBEN et G. DUYCKAERTS pour l'intérêt qu'ils ont porté à ce travail, Monsieur J. GOVAERTS pour l'assistance dans les mesures d'absorption et l'Institut des Sciences Nucléaires pour les subsides qu'il a bien voulu nous accorder.

RÉSUMÉ

La recherche d'une bonne méthode de séparation Rb-Cs, en quantités microchimiques par chromatographie sur cellulose, nous a montré que seul un éluant à base de phénol (équilibré avec H$_2$O ou HCl 2N) permet d'obtenir, de façon simple, des résultats excellents.

Cette séparation reste excellente aussi bien avec des quantités de quelques milligrammes qu'avec des doses extrêmement faibles et nous avons pu l'appliquer à la séparation sélective du ^{137}Cs de fission ,,carrier free'', directement à partir d'une solution nitrique d'uranium irradié.

SUMMARY

A search for a good method of separating Rb-Cs in micro-quantities by chromatography on cellulose has revealed that only with a phenolic eluant (equilibrated with H$_2$O or 2N HCl) can a specially good separation be easily obtained.

This separation remains quite effective from quantities of a few milligrams to "tracer" amounts, and we were able to obtain a selective separation of fission ^{137}Cs "carrier free", directly from a nitric solution of irradiated uranium.

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ZUSAMMENFASSUNG

Auf der Suche nach einer guten mikrochemischen Trennungsmethode von Rb-Cs mittels Chromatographie auf Zellulose hat es sich gezeigt, dass nur Elution mit Phenol (das mit H_2O oder $2N$ HCl gesättigt ist) eine besonders gute Trennung ergibt.

Diese Trennung bleibt sowohl mit Mengen von einigen Milligrammen als auch mit Spuren sehr gut. Es gelang uns, nach dieser Methode das Spaltprodukt ^{137}Cs aus einer bestrahlten Urannitratlösung selektiv abzutrennen.

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ELECTRO-CHROMATOGRAPHY AND THE MOVEMENT OF COMPLEX IONS

by

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Much study has been devoted to the electro-chromatography of inorganic cations since the technique was first recorded in 1951. Separations of many groups of cations have been attempted and several papers have been devoted to examining the factors controlling the movement of inorganic ions during electro-chromatography.

LEDERER AND WARD[1,2] investigated the movement of a large number of metal ions using hydrochloric acid as the carrier electrolyte. The differential movement was attributed to capillary flow of the solvent in the paper, adsorption on the paper and the potential applied. The movement of individual ions was greatly influenced by the concentration of HCl used as the carrier, since for metals which form complexes with chloride ions, the mobility of the ion may change with the chloride concentration.

SATO, NORRIS AND STRAIN[3] examined the electro-chromatographic sequences of inorganic cations with a large variety of electrolytic solutions and found that the sequences were dependent upon the composition of the electrolytic solution and upon the nature and treatment of the porous support. The mechanisms of these variations could be related to many effects, such as the formation of complexed ions in the electrolytic solution, variation of the sorption of ions by the porous support and variation of the activity or degree of dissociation of the migrating ions.

The electro-osmotic flow of liquid which occurs in paper electro-chromatography was investigated by ENGELKE, STRAIN AND WOOD[4] and was attributed to a driving force within the paper. This force was found to depend upon the electrical field, the treatment of the paper and the concentration and nature of the electrolytic solution. The electro-osmotic flow increased with increasing field strength and dilution of the electrolytic solution, and under the conditions employed in these experiments, the electro-osmotic migration exceeded the electrical mobilities of many ions. Thus the mobilities and even the direction of migration of substances examined by electro-chromatography cannot be accurately specified unless the electro-osmotic transport is determined or controlled. Since electro-osmosis is a function of many variables, these authors were pessimistic regarding the possibility of obtaining precise, reproduceable values for the mobility of ions.

The effect of concentration and sorption upon the migration of cations has recently been studied by SATO, NORRIS AND STRAIN[5]. With zones of ions such as Pb and Bi, that are readily sorbed by the paper, the rate of electrical migration was found to be proportional to the concentration and approaches an upper limit as the concentration of the ion approached the ionic concentration of the back-ground electrolytic solution on the paper. Similar results were obtained with comparative paper chromatograms with variation of cation concentration. Many ions, particularly those not sorbed by the paper, migrated at a rate independent of their concentration provided that the concentration was less than that of the electrolytic back-ground solution. With zones of the mixture at concentrations higher than that of the electrolytic solution, the migration decreased with increasing concentrations. At the leading boundaries of the zones, the ions diluted by diffusion and convection migrate rapidly, producing long diffuse leading regions.

The conclusions of these detailed American studies confirm in many respects the validity of the interpretations published by LEDERER AND WARD in the earlier studies. In paper electro-chromatography, the separability of mixtures of various ions depends upon the differential migration rates. These rates have been shown to vary with many conditions such as the nature and concentration of the back-ground electrolytic solution moistening the paper, the treatment and wetness of the paper, the temperature, magnitude of the osmotic effect, the concentration and sorbability of the ion. Since several of these factors are difficult to control in analytical studies, the ideal condition for separations involves the formation of at least one ion of opposite electrical sign to other ions present.

This condition may be obtained by electro-chromatographing mixtures of complex ions. The stability of the complex could have a profound influence on both the type and charge of ion attracted by the applied potential and the sorption of ions by the paper could vary between complex and simple salts.

We have studied the movement of metal nitrates on paper moistened with potassium nitrate under varying conditions of relative concentration, in order to make a preliminary study of the analytical possibilities of separations through added complex ions.

EXPERIMENTAL

The glass-plate technique recorded by Lederer and Ward was adopted using Whatman No. 120 Spot Reaction Filter Papers and either molar, deci-molar, or centi-molar KNO_3 as the carrier electrolyte on the paper. The ends of the paper not enclosed by the glass plates dipped into reservoirs of the carrier electrolyte and a potential equivalent to 5 volts/cm of paper was applied for seventy minutes through two carbon electrodes immersed in the reservoirs.

With the dilute carrier solutions little heating was observed but with the molar carrier cooling of the glass plates was found desirable.

M, $M/10$ and $M/100$ solutions of the nitrates of Ag, Pb, Hg, Bi, Cd, Cu, Fe, Mn, Ni and Co were prepared and approximately 0.004 ml quantities were spotted in the centre of the filter paper and the relative rates of movement and size of resultant spots were compared using different concentrations of carrier electrolytes.

Complex ions of the metals were formed by diluting the molar nitrates to deci-molar with excess of the following reagents: NH_4OH, alkaline KCN, KCNS, weakly acid and weakly alkaline solutions of disodium ethylenediaminetetraacetate. Spots of these solutions (including precipitates formed) were treated similarly to the nitrates using $0.1 M$ KNO_3 as carrier electrolyte.

Where necessary, complex ions were decomposed by spraying with acid before the cations were finally located with H_2S and other standard spot test reagents.

The results of the practical experiments are summarized in Tables I and II. The ionic movements tabulated were obtained by measuring the distance between the centre of the original spot and the centre of the spot located after electro-chromatography. In many cases ionic movement was accompanied by diffusion and expansion of the zone size and an indication of the increase in size is given by the numbers in parentheses shown on the tables. These numbers represent the approximate multiple increase and in the majority of expansions, the original circular area (of approx. 50 sq. mm) was greatly elongated in the direction of the flow of ions.

The approximate spot areas are considered to be so important that they cannot be overlooked when using ionic movement for the purposes of predicting analytical separations since with large areas, one particular cation can be found in many positions on the paper and will readily interfere with other ions of larger or smaller ionic mobility, thus preventing clear boundaries.

Occasionally, complexing agents formed precipitates on the addition of the cation and this fact is recorded in Table II. In some cases cations from the precipitated material moved completely during electro-chromatography while other compounds gave two spots implying that two species existed in the complexed solution.

Under the standard conditions used in this experiment, the degree of reproducibility of results was highly satisfactory and the figures recorded are the mean values of several tests.

DISCUSSION

Nitrates were chosen as the anion for the metals and carrier electrolyte since they were believed to have a minimum tendency to form anionic complexes in simple salt solutions. Under the comparative conditions of the electro-chromatograms the variation in movement of the simple cations could thus be attributed to the major influence of a single factor such as increased diffusion with dilute carrier electrolytes or increased sorption with decreasing concentration of cation present.

Electro-osmotic flow has been shown to increase with increasing dilution of carrier electrolyte[4] and the variation in cation movement with increasing flow is shown by the horizontal rows of figures in Table I. From these results it may be tentatively concluded that direct flow of solvent has had little effect on actual forward movement of the cations but the flow has assisted the difusion of the soluble metal salts. The more dilute the carrier, the greater the tendency for the cations under test to diffuse throughout the solution. This diffusion will give the equivalent of low concentrations of cation over wider surfaces of paper which may facilitate greater adsorption and explain the smaller movement observed for most ions in 0.01M KNO_3 carrier solutions. The increased diffusion is readily discerned by comparing the relative spot areas of similar amounts of metal salt in different carrier electrolytic solutions. The diffusion of the metal salt into the carrier would be retarded by having a higher concentration of salt in the carrier as is shown by the results tabulated in Table I.

Previously reported acceleration[2,4] did not occur and ionic mobility was influenced more by the secondary effects of diffusion.

Other workers[2,5] have emphasized the important role of sorption on the movement of inorganic ions and their conclusions have been confirmed by our study. Some ions such as Ag^+, Pb^{+2}, Bi^{+3}, Hg^{+2} and Fe^{+3} are strongly sorbed by the paper and their movement is largely dependent on the concentration of cation present. Paper, like other adsorbents may be considered capable of adsorbing different quantities of material per unit weight of paper. Where adsorbing capacity for a metal is high, *e.g.* Bi^{+3} and Hg^{+2}, the original spot remains unmoved even at high concentrations. Where adsorbing capacity is smaller, high concentrations of a cation may move under the influence of the electrical field until the dilution is sufficiently great to allow complete adsorption over a wider area. This effect is shown by Ag^+ and Pb^{+2}. Some ions are apparently little adsorbed and have similar migration under all conditions *e.g.* Mn^{+2}, Ni^{+2} and Co^{+2}. With high concentrations of carrier electrolyte,

TABLE I

THE EFFECT OF VARIATIONS IN THE CONCENTRATION OF CARRIER ELECTROLYTE AND METAL SALT ON THE MOVEMENT OF CATIONS

Spotted salt		*Concentration of KNO_3 carrier*			*Remarks*
		molar	*0.1 molar*	*0.01 molar*	
M	$AgNO_3$	+38 mm (13)	+39 mm (13)	+24 mm (17)	The spots which moved were comet shaped, tailing back to zero. With *M* $AgNO_3$ much $Ag+$ was concentrated at the leading edge.
0.1*M*	,,	+11 ,, (2)	+17 ,, (6)	+13 ,, (4)	
0.01*M*	,,	+2 ,, (1)	0 ,, (1)	0 ,, (1.5)	
M	$Pb(NO_3)_2$	+21 ,, (4)	+31 ,, (13)	+25 ,, (18)	Diffuse and cometed spots were obtained when the [Pb^{+2}] > the molarity of the carrier electrolyte
0.1*M*	,,	+12 ,, (3)	+14 ,, (4)	+16 ,, (11)	
0.01*M*	,,	+2 ,, (1)	+27 ,, (2)	+9 ,, (4)	
M	$Hg(NO_3)_2$	+8 ,, (4)	+11 ,, (5)	+13 ,, (5)	The ions adsorbed strongly on the paper but some movement occurred when [Hg^{+2}] > the KNO_3 molarity
0.1*M*	,,	+8 ,, (3)	+1 ,, (2)	+5 ,, (3)	
0.01*M*	,,	0 ,, (1)	0 ,, (1)	+2 ,, (2)	
M	$Bi(NO_3)_3$	0 ,, (1)	+2 ,, (2)	+2 ,, (2)	The bismuth salt was very strongly adsorbed by the paper
0.1*M*	,,	0 ,, (1)	0 ,, (1)	0 ,, (1)	
0.01*M*	,,	0 ,, (1)	0 ,, (1)	0 ,, (1)	
M	$Cd(NO_3)_2$	+36* ,, (6)	+18 ,, (7)	+26 ,, (22)	High concentrations of Cd salt diffused over broad areas extending from the original spot
0.1*M*	,,	+50* ,, (9)	+15 ,, (4)	+30 ,, (6)	
0.01*M*	,,	+49* ,, (1)	+14 ,, (2)	+30 ,, (2)	
M	$Cu(NO_3)_2$	+27 ,, (3)	+30 ,, (10)	+24 ,, (21)	Similar to $Pb(NO_3)_2$
0.1*M*	,,	+21 ,, (3)	+26 ,, (4)	+17 ,, (7)	
0.01*M*	,,	0 ,, (1)	+27 ,, (1)	+11 ,, (2)	
M	$Fe(NO_3)_3$	+7 ,, (4)	+16 ,, (9)	+4 ,, (2)	The iron was strongly adsorbed by the paper and observed migration was due to tailing from the original spot
0.1*M*	,,	+13 ,, (3)	+1 ,, (2)	+4 ,, (2)	
0.01*M*	,,	+1 ,, (1)	+2 ,, (1)	+0 ,, (1)	
M	$Mn(NO_3)_2$	+40* ,, (1)	+30 ,, (2)	+32 ,, (11)	The cations migrated in fairly compact zones
0.1*M*	,,	+44* ,, (6)	+30 ,, (1)	+36 ,, (2)	
0.01*M*	,,	+48* ,, (1)	+26 ,, (1)	+37 ,, (1)	
M	$Ni(NO_3)_2$	+27 ,, (6)	+26 ,, (11)	+23 ,, (19)	The Ni^{+2} migrated as elongated ovals extending from above the original spot
0.1*M*	,,	+26 ,, (4)	+27 ,, (4)	+20 ,, (14)	
0.01*M*	,,	+22 ,, (1)	+30 ,, (1)	+18 ,, (4)	
M	$Co(NO_3)_2$	+40* ,, (7)	+30 ,, (2)	+27 ,, (16)	Similar to nickel
0.1*M*	,,	+52* ,, (8)	+29 ,, (2)	+34 ,, (8)	
0.01*M*	,,	+52* ,, (2)	+29 ,, (1)	+26 ,, (3)	

* Heating effects may have influenced the movement of these ions.

The results in parentheses represent the approximate increase in area of spot caused by electrochromatography

TABLE II

THE EFFECT OF COMPLEXED FORMS ON IONIC MOVEMENT

Metal	*Aqueous nitrate*	*Complexing agent present*				
		Alk. KCN	*KCNS*	*NH$_4$OH*	*EDTA*	
					pH 3	*pH 9*
Ag	+17 mm (6)	−22 mm (1)	0* mm (1)	+22 mm (7)	0* & −8 mm	−12* mm (7)
Pb	+24 ,, (4)	0* ,, (1)	+24* ,, (4)	+15* ,, (2)	5* & −15 ,,	−20 ,, (2)
Hg	+1 ,, (2)	−12 ,, (3)	−8* & 0 mm	0* ,, (2)	* − 2 ,,	0* & −17mm
Bi	0 ,, (1)	0 ,, (1)	0 mm (1)	0* ,, (1)	0 & − 3 mm	−10 mm (5)
Cd	+15 ,, (4)	−7 ,, (2)	+15 ,, (4)	+8 ,, (1)	+8 & − 9 ,,	+6 & −10mm
Cu	+26 ,, (4)	−24 ,, (1)	+22 ,, (1)	+16 ,, (1)	+9 & − 13mm	0 & −20 ,,
Fe	+1 ,, (2)	0* & −45 mm	+4 ,, (2)	0* ,, (1)	0 mm (1)	−15 mm (7)
Mn	+30 ,, (1)	−11 mm (2)	+28 ,, (2)	+11 ,, (2)	+5 ,, (1)	0 ,, (1)
Ni	+27 ,, (4)	−37 ,, (7)	+33 ,, (7)	+15 ,, (2)	+17 ,, (5)	+24 ,, (8)
Co	+29 ,, (2)	−28 ,, (4)	+21 ,, (8)	+4 ,, (3)	+18 ,, (8)	+6 ,, (4)

* Indicates that a precipitate was present in the spotted solution.
The carrier electrolyte was $0.1M$ KNO_3 and the concentration of metal ions in the spot solution was $0.1M$.

there is obviously a "salting effect" which decreases the solubility of small quantities of metal ions and thus increases the absorption (*cf.* $0.01M$ Ag^+, Cu^{+2} and Fe^{+3} on M KNO_3 carrier). Conversely, high concentrations of carrier electrolyte will tend to reduce the adsorptive capacity of unit area of paper and hence concentrated solutions of cations will be free to move with less retardation due to sorption and under ideal conditions may move as concentrated zones.

The effects of complex ions on the movement of cations was studied by spotting the complex (in the presence of a small excess of reagents) directly on the paper. This technique was considered preferable to that of SATO, NORRIS AND STRAIN[3] in which the complexing agent was used as the carrier. The latter method has the advantage of ensuring the presence of complexing agent at all times and hence equilibrium will favour the continued existence and movement of a metal complex. It has been shown[6,7] that in simple chromatographic separations, the degree of movement and size of spot can be proportional to the relative concentration of cation and complexing agent unless the latter is present in large excess. Thus for uniform migration, a concentrated solution of complexing agent is desirable. This could lead to heating of the paper due to high current flow. Heating would increase liquid flow and ionic mobilities.

The addition of the complexed salt to a neutral carrier involves effects due to the different stabilities of compounds. Indications from the preliminary studies shown in Table II are that the stabilities of complexes during electro-chromatography can be different from those anticipated from standard figures of stability constants.

The anionic cyanide complexes of Ag, Cu, Ni and Co all moved similar distances while the weaker complexes of Hg, Cd and Mn were transported less than half the distance of the very stable complexes.

In the presence of KCNS, Hg^{+2} was the only cation which tended to move as an anionic complex. With the exception of silver (precipitate of AgCNS), the movements observed with other cations were almost identical with the behaviour of the simple nitrates under similar conditions.

Of the amine complexes, silver amine moved slightly more than the simple ion probably due to a reduced tendency for sorption while the movement of the amines of Cu, Cd, Ni and Co were appreciably smaller. Since the effect was much larger with Co, this retardation could be attributed to the smaller charge per unit area of the co-ordinate complex molecule.

Complexes of cations and di-Na ethylenediaminetetraacetate are usually very stable but it is recorded[8] that the stability can be influenced by the ionic strength of the solution and the pH of the solution. The instability brought about by this salt effect in electro-chromatograms is clearly illustrated by the figures in Table II. Many cations yielded double spots, one anionic (the complex) and one cationic (the simple ion). Normally, all the cations tested form strong anionic complexes with EDTA but it will be observed that two of the most stable, *viz.* Ni and Co, are apparently completely decomposed and only the simple cation is attracted by the applied potential. The resultant spots are very diffuse but the total movement is only slightly less than that of the similarly treated simple salt.

Thus while the formation of complex ions may be used to separate cations which tend to react from those that do not (using the technique of SATO[3]), further investigation of the "salting effect" as shown in EDTA solutions may lead to separations within a complexed group.

CONCLUSIONS

The investigation has confirmed that the movements of inorganic cations during electro-chromatography are influenced by the concentration and type of cations present, the concentration of carrier electrolyte, the temperature and sorptive capacity of the paper for the cation.

The results obtained place a slightly different emphasis on the role of the carrier electrolyte. This electrolyte can reduce the migration by "salting out" small concentrations of cations or increase the movement by occupying active centres on the paper thus reducing sorption of the cation by the paper. Dilute carrier solutions promote electro-osmotic flow in the paper and allow concentrated test spots to diffuse over large areas. In the presence of complex ions, the ionic strength of the carrier may be sufficiently great to cause decomposition of otherwise stable ions.

SUMMARY

It is apparent that, in electro-chromatographic separations, the change of area undergone by the initial spot of test solution plays a part in the final interpretation of results almost as important as the actual movement of the centre of the spot.

Several interesting facts have emerged from this research concerning the role of the carrier electrolyte on the movement, the spot size, and the stability of complex salts.

RÉSUMÉ

Il ressort que dans les séparations électrochromatographiques, le changement de l'étendue de la tache initiale d'une solution à examiner joue un rôle dans l'interprétation finale des résultats, presque aussi important que celui du mouvement même du centre de la tache.

Ces recherches mettent en évidence plusieurs faits intéressants, concernant l'influence de l'électrolyte de base sur le mouvement, les dimensions de la tache et la stabilité des sels complexes.

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ZUSAMMENFASSUNG

Es ist augenscheinlich, dass bei elektrochromatographischen Trennungen, die Oberflächenänderung des ursprünglichen Flecks der Testlösung bei der Endauslegung der Ergebnisse eine beinah ebenso wichtige Rolle spielt, wie die Wanderung des Fleckmittelpunktes selbst.

In dieser Untersuchung treten verschiedene interessante Tatsachen hervor, die sich auf die Wirkung des Trägerelektrolyten auf die Wanderung, Fleckgrösse und Beständigkeit der komplexen Salze beziehen.

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INORGANIC ANALYSIS IN ORGANIC SOLVENTS

I. SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM FOLLOWING A CHROMATOGRAPHIC SEPARATION

by

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INTRODUCTION

Whereas several cations have been determined spectrophotometrically by measurement of the colour intensities of their 8-hydroxyquinolates in organic solvents[1-5], no similar method for the determination of chromium has been reported. Chromium forms a yellow 8-hydroxyquinolate and 8-hydroxyquinaldate* that are not easy to precipitate quantitatively from pure chromium solutions and which possess spectral properties similar to those of several other such metal complexes and to those of the reagents themselves.

This paper describes a method in which the 8-hydroxyquinolate, or better, the 8-hydroxyquinaldate complexes of chromium are separated from those of most other metals by selective adsorption on activated alumina from organic solvents, especially benzene-chloroform 1:1 solutions. The chromatographic column is unelaborate, and is rapidly prepared. After separation, the chromium is determined by measuring the optical density of the solution at the adsorption maximum of the complex employed. The solutions of both complexes obey the Beer-Lambert law. Essentially the method is micro, but to avoid sampling errors, *e.g.*, where comminution of the sample is difficult, it is necessary to take macro starting weights and obtain the determination sample by taking a suitable aliquot. The method is applicable to the determination of chromium in a very wide range of materials, including ferrous and non-ferrous alloys, chromium ores and other mineral matter. The chromium, unless present only as a very minor constituent, may be determined to within ± 0.2 μg, *i.e.*, to within about 1 part in 200 in the average case.

Organo-chromium complexes do not readily and quantitatively form conveniently filterable precipitates, and the 8-hydroxyquinaldate is considerably more difficult to collect than the 8-hydroxyquinolate[6]; but in the presence of sufficient ferric iron, chromium is precipitated quantitatively and in an easily filterable condition by either complexing agent. The amount of iron present in the precipitation solution must be at least twice the amount of chromium, and should also be at least equal to the combined weights of all other metals. Those metals which form crystalline complexes, *e.g.*, cobalt and nickel, inhibit rather than assist the complete precipitation of chromium. In the case of ferrous alloys and iron ores, sufficient iron is present for all the chromium to be precipitated, but in some other cases, addition of about 5 mg of ferric iron is necessary before precipitation.

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* The term "8-hydroxyquinaldate" (*cf.* 8-hydroxyquinolate) is used to describe the complexes of 8-hydroxyquinaldine, in order to avoid confusion with quinaldinates, the salts of quinaldinic acid.

Because of the relative ease of precipitation, 8-hydroxyquinoline is recommended as the better reagent provided that aluminium, cobalt and vanadium are absent: the 8-hydroxyquinolates of these three metals are not completely retained on alumina from benzene-chloroform 1 : 1. Vanadium and aluminium, however, cause no difficulties when present only in relatively minor amounts. Cobalt and pentavalent vanadium are completely retained on alumina when 8-hydroxyquinaldine is used as reagent, but tetravalent vanadium is not, and interferes in the spectrophotometric determination of chromium. Special circumstances arise when only small amounts of chromium are present in the presence of much vanadium, as for example in the analysis of ferrovanadium. In this case, both vanadium and chromium are oxidized by digestion with ammonium persulphate, the excess of persulphate being destroyed by further boiling. The small amount of dichromate is reduced by and combines with the 8-hydroxyquinaldine, while all the vanadium remains in the pentavalent state. The digestion time must be extended by 10-20 minutes in this case; the oxidation products of the reagent appear to have no adverse affect on the analysis.

Since 8-hydroxyquinaldine does not react with aluminium, this metal will, when present, appear in the precipitate as its hydrated oxide and efforts should be made to remove excessive amounts of this element before the solution is made ammoniacal, otherwise the bulky hydrated oxide is an inconvenience. Tartaric acid must not be added to prevent precipitation of hydrated alumina because it also prevents complete precipitation of chromium.

The developing solvent, benzene-chloroform 1 : 1, or when fire hazards preclude the use of benzene, trichloroethylene-chloroform 1 : 1, is chosen so that all the chromium appears in the eluate and all other metals, apart from known interferences, are retained in the column. Chromium is completely retained on alumina from pure benzene or trichloroethylene, while some other metals are not completely retained from pure chloroform[7]. Alcohol dissolves traces of alumina from the column, but the small percentage of alcohol used as a preservative in the chloroform has no adverse affect, and, indeed, it must not be removed, otherwise the photochemically produced hydrogen chloride decomposes the organo-metallic complexes, and low results are obtained in the chromium determination.

EXPERIMENTAL PROCEDURE

(i) *Size of the sample*

The amount of chromium which is passed through the column should be between 0.01 and 0.3 mg (the extreme lower limit is about 2 μg, but the chromium can only be measured to within ± 0.2 μg; the upper limit may be raised to 0.6 mg by diluting the eluate to 100 ml instead of 50 ml). The total weight of metals to be adsorbed on the column should be between 1 and 5 mg, although up to 10 mg can be handled by using longer columns. In some cases, such as ferrous alloys and iron ores, which contain sufficient iron to co-precipitate the chromium, a sample weight containing 5 mg of metals may be taken provided that sampling errors are avoided and the chromium content is not above 10%; all the sample is precipitated and passed through the column. The taking of aliquots is recommended in the following circumstances: (a) when comminution of the sample is impossible, or segregation is significant, (b) when the chromium content is above 10% so that a 3-5 mg sample contains more chromium than may be passed through a column. In this case, an aliquot is taken of the aqueous solution and ferric iron is added before precipitation.

If the alloy is mainly iron and very low in chromium, a much larger sample may be taken, and most of the iron removed by ether extraction from a solution 6*N* with respect to hydrochloric acid[8]. In the case of non-ferrous alloys, the sample weight must be chosen, bearing in mind the smallest weight representative of the whole, the expected chromium content and the amount of iron to be added.

(*ii*) *Attack of the sample*

(a) *Alloys not attacked by alkalies*

Cover the sample with water, add 5-20 ml of dilute (1:1) sulphuric acid and warm gently to dissolve the metal. If the attack is very slow (as with nickel alloys), add 10 ml of concentrated hydrochloric acid to speed dissolution, but chloride ions must be removed by evaporation to fuming before the addition of oxidizing agents in order to avoid losses as chromyl chloride; then dilute to 20-30 ml with water. Add 10 ml of concentrated nitric acid, evaporate to fumes of sulphuric acid, cool, dilute to 20-30 ml with water and warm gently until all metal-salts have dissolved. If resistant carbides are present, fuming with sulphuric-perchloric acid may be necessary: if this is done, boil the solution for ten minutes after dilution of the residue. If the ferric concentration is excessive, make 6*N* with respect to hydrochloric acid by adding an equal volume of the concentrated acid and extract once with an equal volume of ether. Boil off the ether from the aqueous layer before precipitating the organic complexes. Sufficient ferric ions remain to ensure complete precipitation of the chromium complexes.

(b) *Aluminium and other alloys attacked by aqueous alkali*

If the alloy is rich in aluminium, zinc or other metal which dissolves in alkalies (or water), cover the sample with hot water and add 10% sodium hydroxide, a little at a time, until the metal is completely attacked. The weight of sample must be chosen according to the proportion of alkali-insoluble metals. Filter off the alkali-insoluble residue which invariably contains all the chromium; wash with 1% sodium hydroxide and then with water. Dissolve the residue in 20 ml of dilute (1:5) sulphuric acid, with additions of concentrated nitric acid if necessary. The solution is evaporated to fuming and the filter paper is destroyed by further small additions of nitric acid, and the fuming is continued to remove traces of volatile mineral acids.

(c) *Ores, Minerals, etc.*

Many minerals such as haematite and carbonates may be partially attacked with dilute (1:1) hydrochloric acid, those rich in silica should be attacked with hydrofluoric-nitric acid mixture. Any residue which cannot be attacked by acids must be fused with five times its weight of sodium peroxide in an iron crucible. This procedure is the only one suitable for attacking chromite unless it is virtually free from silica, when perchloric acid may be employed[9]. When the fusion method of attack is used, leach out the fused cake with water after cooling, and acidify with sulphuric acid. In those cases where a wet attack is possible, all hydrofluoric and nitric acids must be removed by fuming with 10 ml of sulphuric acid.

(iii) *Reduction of* Cr^{VI} *to* Cr^{III}

The solution to be precipitated with 8-hydroxyquinoline or 8-hydroxyquinaldine must not contain appreciable amounts of chromate or the chromium will not be precipitated quantitatively. In those cases where all the chromium is oxidized to the hexavalent state, as when fuming with perchloric acid or fusion with sodium peroxide are necessary, the chromate is reduced by boiling the resulting dilute sulphuric acid solution with 5 ml of alcohol for 15 minutes.

(iv) *Precipitation of the organic complexes*

The total weight of metals present in the solution should be 3-5 mg (excluding aluminium) or 10-50 mg if an aliquot is to be taken of the chloroform solution. Dilute the solution, if necessary, to 20 ml, heat to 70° C and add dilute (1:1) aqueous ammonia drop by drop, with stirring, until a faint permanent precipitate is formed; dissolve this with a drop of dilute sulphuric acid and proceed as follows:

(a) 8-Hydroxyquinoline as reagent: add 10 ml each of 2% 8-hydroxyquinoline in 2*N* acetic acid, *N* sodium hydroxide and 4*N* ammonium acetate in that order, with continuous stirring.

These quantities of reagents are sufficient for up to 10 mg of metals of average atomic weight 50 and valency 2-3, and proportionately more should be used for larger amounts. Adjust the pH to 8 by the addition, drop by drop, of dilute (1:1) aqueous ammonia, boil for one minute, digest with occasional stirring for ten minutes, or until the precipitate is coagulated and the liquid clear yellow.

(b) 8-Hydroxyquinaldine as reagent: prepare a diluted reagent solution by taking a volume of 2% 8-hydroxyquinaldine in 2*N* acetic acid such that there is an excess of 1-2 ml over the amount required to combine with all the metals present, and dilute to 10 ml (or 20 ml) with 2*N* acetic acid. If a larger excess is used, the reagent separates as an oil, causing the precipitate to become pasty, in which case all the chromium is not precipitated. Add the diluted 8-hydroxyquinaldine solution to the weakly acid solution of the metals, followed by 10 ml (or 20 ml) each of *N* sodium hydroxide and 4*N* ammonium acetate with stirring. 10 ml quantities of reagents are sufficient for up to 10 mg of metals (excluding aluminium); 20 ml should be used for larger amounts. Adjust the pH to 6 by the addition, drop by drop, of dilute ammonia or sulphuric acid and digest the solution at 70-80° C, with frequent stirring, until the precipitate has coagulated and the liquid is clear yellow.

Collect the precipitate in a sintered glass crucible and wash it with 20-30 ml of hot water. It is unnecessary to transfer quantitatively the adhering precipitate from the beaker to the filter. A Schwarz-Bergkampf type filter beaker of 100 ml capacity, if available, is most convenient, thus enabling the precipitation, and solution of the complexes in chloroform to be carried out in one vessel. Dry the crucible and beaker at 105-110° C.

Dissolve an 8-hydroxyquinaldate precipitate by drawing 20-30 ml of hot chloroform through the crucible, wash the beaker with chloroform and combine the solutions. As 8-hydroxyquinolates do not dissolve so readily, transfer these precipitates to the precipitation beaker, wash the crucible with 40-50 ml of hot chloroform and add this to the beaker containing the precipitate. Keep the mixture hot until all the solid has dissolved. Examination over an intense light source is a suitable means of observing when solution is complete. If an aliquot is to be taken of the chloroform solution, dilute it, when cold, to exactly 100 ml with chloroform.

(v) *Preparation of the chromatographic column*

(a) Tube to hold the alumina column

The tube should be 5-6 mm internal diameter, about 30 cm long, with a wider portion at the top so that it will hold at least 30 ml above the alumina. A ground glass joint just above the stopcock is desirable to facilitate cleaning. The spring-loaded stopcock barrel must be of good quality and should be lightly smeared with silicone grease.

(b) Preparation of the column

Pour 5 ml of benzene-chloroform (1:1) into the tube, push a piece of cotton wool down to the bottom of it with a glass rod, and fill it with the solvent mixture to the top of the narrow part. If the tube has aquired an electrostatic charge, place a concentric wider tube over it. Pour in sufficient dry, dust-free sand through a long funnel to form a layer 1 cm deep on top of the cotton wool, followed by a quantity of activated alumina, as the dry powder, sufficient to form a column 4 cm high. When the alumina has settled, add a second, similar quantity. The tube should be tapped gently after each addition of sand or alumina to level the top of the column. The layer of fines in the middle of the alumina column so formed ensures retention of traces of any complexes, except chromium, which may pass the top of the column. A column 8 cm high is sufficient for up to 20 mg of complexes; proportionately longer columns are necessary for larger amounts.

(vi) *Chromatographic separation and determination of chromium*

If the whole of the chloroform solution of the precipitate is to be passed through the column, evaporate it to 10-12 ml. If the weight of precipitate exceeds 50 mg, evaporate to 30 ml. In either case add an equal volume of benzene. Alternatively, take a 10 ml aliquot from 100 ml and add 10 ml of benzene. Mix well, run the liquid out of the column, leaving 1 cm above the alumina and add the solution of the metallic complexes; rinse the beaker with the solvent mixture and add the washings to the column. Place a clean, dry 50 ml or 100 ml graduated flask beneath the column (the 100 ml flask is necessary when the volume of chloroform solution of the complexes exceeds 12 ml, and when more than 0.1 mg of chromium is present as its 8-hydroxyquinolate), open the stopcock and let the liquid run into the flask at a rate not exceeding one drop per second. As soon as all the liquid has passed through, wash the column with benzene-chloroform (1:1) until the flask is full to the mark. Stopper the flask and mix well. Measure the optical density of the yellow solution spectrophotometrically at 425 mμ (8-hydroxyquinolate) or 410 mμ (8-hydroxyquinaldate). Choose the path length according to the colour-intensity of the solution.

(vii) *Standards*

Prepare a standard chromic solution from A.R. potassium dichromate or electrolytically refined chromium metal. To various aliquots of this solution add 10-20 mg of iron as ferric sulphate solution and proceed exactly as described above for both reagents. Plot graphs of optical density against mg of chromium in 50 or 100 ml, which will be straight lines from zero to as far as it is possible to measure optical densities accurately.

DISCUSSION

Interferences and sources of error

To obtain accurate results, two conditions must be fulfilled:

(a) All the chromium in the aqueous solution must be precipitated as the organic complex. This is ensured by having sufficient ferric iron present and at least most of the chromium in the trivalent state, and by using the correct excess of reagent.

(b) All the chromium must elute from the column, and all the other metals must be completely retained on it.

All the chromium will elute, if the right proportions of benzene and chloroform are used. For most activated alumina, a 1 : 1 mixture by volume is satisfactory. The metals which are not completely retained on the column under the conditions of the determination are as follows:

8-Hydroxyquinolates: aluminium and vanadium (except in very minor amounts) and cobalt cause high results. Aluminium 8-hydroxyquinolate is not completely retained on activated alumina from 1 : 1 benzene-chloroform and causes a marked interference on account of its bright yellow colour and strong fluorescence. It is also formed if 8-hydroxyquinoline is passed through the column. Owing to the alcohol present in commercial chloroform, any vanadium 8-hydroxyquinolate will be present in the red form[10]. This is not adsorbed on alumina, and may elute as a red solution if present in large amount; but in contact with alumina, it decomposes, forming an aluminium 8-hydroxyquinolate. Anhydrous cobalt 8-hydroxyquinolate is completely retained on the alumina column, but its dihydrate is not adsorbed at all. But even when dehydrated at 120° C, sufficient moisture is always present in the solvents to cause at least a partial re-formation of the dihydrate.

8-Hydroxyquinaldates: of the metals investigated, namely Fe^{III}, Al, U, Ce, Ti, Ni, Cu, Mo, Mn, Co, Th, Zn, V^{V}, W, Ga, In, Tl, and alkaline earths, none have been found to cause any interference in the chromium determination. Aluminium does not form an 8-hydroxyquinaldate, and the cobalt derivative is completely retained in the column, probably because it does not form a hydrate. The 8-hydroxyquinaldate of pentavalent vanadium does not form a red coloured solution with the amount of alcohol present in commercial chloroform, and it is completely retained on alumina with no apparent decomposition. However, all the vanadium must be in the pentavalent state, as the 8-hydroxyquinaldate of tetravalent vanadium is only weakly adsorbed on alumina, and would consequently cause high results.

Results — Accuracy and precision

The following tables illustrate the wide range of materials and chromium concentrations which can be analysed by the above method.

(a) *8-Hydroxyquinoline as reagent*

Material		*Analytical results %*	*Mean %*	*Chromium by standard methods %*
Ferrochromium	BCS 203	69.2, 69.4, 69.5, 69.0	69.3	69.0
Cr-V Steel	BCS 165	0.87, 0.85, 0.89, 0.90	0.87	0.86
Cr-Ni-Ti Steel	BCS 209	18.30, 18.25, 18.26	18.3	18.7
Cr-Ni Steel	BCS 189	0.69, 0.65, 0.68	0.67	0.68
Cr-Ni-Mo Steel	BCS 219	0.82, 0.82, 0.83	0.82	0.82
Co-V Steel	BCS 167	6.69, 6.81	6.75	3.32
Co-V Steel	BCS 167	3.33, 3.30	3.32*	3.32
Cr-V-W-Co Steel	BCS 166	7.01, 7.08	7.04	3.01
C Steel	BCS 163	0.029, 0.027	0.028	0.03
Alloy Cast Iron	BCS 173	3.90, 3.81	3.86	3.97
Alloy Cast Iron	BCS 172	0.385, 0.392	0.39	0.41
Cr-V Steel	BCS 224	1.61, 1.57	1.59	1.46
Low Alloy Steel	BCS 257	1.71, 1.71	1.71	1.72
Inconel		13.5, 13.5	13.5	14.0
Brightray		20.6, 20.9	20.7	21.0
Hydra 80-20		20.20, 20.35	20.3	20.5

* Figure obtained after group separation of the cobalt.

(b) *8-Hydroxyquinaldine as reagent*

Material		*Analytical results %*	*Mean %*	*Chromium by standard methods %*
Ferrochromium	BCS 204	71.3, 71.1	71.2	71.4
Kanthal		23.8, 24.0	23.9	23.3
Cobalt Steel	BCS 167	3.20, 3.38	3.29	3.32
Haematite		2.38, 2.33	2.36	2.38
Chromite		30.73, 31.20, 30.94	31.0	30.90
Aluminium Alloy		0.077, 0.074, 0.075	0.075	0.07
Aluminium Alloy		0.020, 0.019, 0.020	0.020	0.02
Ferrovanadium		0.073, 0.078	0.075	—

The analytical results given in the above tables are those of determinations on true replicates on the original sample, duplicate aliquots of a chloroform solution of the precipitate gave almost identical results. Agreement between replicates is seen to be very good in most instances and the results close to those of analyses by classical methods. In those cases where there is an appreciable deviation among replicates, the samples were all metals which could not be crushed, and which therefore admit the possibility of segregation and sampling errors.

A statistical analysis was made of a ferrochromium containing 72.1% chromium (BCS 203/1). An alloy with a high chromium content was chosen, as this provides a more searching test of the precision of the method. Triplicate determinations were made on ten samples; the mean of the thirty results was 72.13%, with a mean deviation of ± 0.6%. 8-Hydroxyquinaldine was used as reagent.

(c) *Analysis of ferrovanadium*

No figure is given in table (b) for the determination of chromium in ferrovanadium by standard methods as no sufficiently accurate method is known, and results were judged by comparison with synthetic mixtures. Two solutions were prepared:

A. A solution containing iron and vanadium in the same concentration as would be given by 0.2 g of a ferrovanadium containing 35% vanadium in 250 ml.

B. A solution containing 0.01734 g of chromium as potassium dichromate in one litre.

Then 5 and 10 ml portions of B were added to 25 ml portions of A and the mixture was precipitated with 8-hydroxyquinaldine. The results are given in the table below. In part (1) the dichromate was reduced by boiling with 1 ml of alcohol. In part (2) smaller volumes of B were added, and the dichromate was reduced by the 8-hydroxyquinaldine.

	B added to 25 ml of A *ml*	*Chromium added* *mg*	*Chromium found* *mg*
(1)	0	0	0.005
	5	0.0867	0.090
	10	0.173	0.176
(2)	0	0	0.000
	1.25	0.0217	0.022
	2.5	0.0433	0.044

Notes on reagents and instruments

(a) *Benzene, chloroform and trichloroethylene*: any reagent grade solvents may be employed, but they should be dried over calcium chloride before use. Chloroform and trichloroethylene containing hydrogen chloride or phosgene must never be used, as these impurities decompose the organic complexes. The alcohol added to the chloroform as a preservative must not be removed, and all the chloroform used in any one determination must be drawn from the same stock bottle. When aliquots are taken of the chloroform solution, the bulk of this solvent may be recovered by distillation and used again without further purification, but alcohol, up to 1% by weight, may have to be added occasionally to prevent photodecomposition. In order to ensure that no change in light transmittance at 410 or 425 mμ occurs when the mixed solvent is passed through an alumina column, a blank test should be made on the fresh and eluted solvent.

(b) *8-Hydroxyquinoline*: it is desirable to use analytical reagent grade material, but any good laboratory reagent grade will suffice.

(c) *8-Hydroxyquinaldine*: the commercial material is expensive and is impure. This reagent may be prepared cheaply by the method described by MERRITT AND WALKER[11], with the modification that the vacuum distillation of the steam-distilled product is omitted, resulting in an increase in yield from 5.2% to 54%, based on the amount of *o*-aminophenol hydrochloride used.

(d) *Activated alumina*: all the work described in this paper has been based on the Peter Spence product, Type H (100-200 mesh). This alumina requires no further activation before use, but must be stored in a tightly closed container. Its activity is between Brockmann Grades I and II[12].

(e) *Spectrophotometer*: The optical density measurements were made on a Unicam S.P. 600 Spectrophotometer.

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SUMMARY

A new method is described for the determination of chromium. In a suitable solution, trivalent chromium is precipitated as its 8-hydroxyquinolate, or 8-hydroxyquinaldate, in the presence of trivalent iron. The dried precipitate is dissolved in chloroform, and the solution, diluted once with benzene, is passed through an activated alumina chromatographic column. The optical density of the eluate, containing the chromium complex only, is measured at 410 or 425 mμ with respect to the solvent. Aluminium, vanadium and cobalt interfere when 8-hydroxyquinoline is used as reagent; but when 8-hydroxyquinaldine is used, the method is unequivocal.

RÉSUMÉ

Une nouvelle méthode est décrite pour le dosage du chrome. Dans certaines conditions, le chrome(III) peut être précipité sous forme de 8-hydroxyquinoléate ou de 8-hydroxyquinaldate,

en présence de fer(III). Le précipité séché est dissous dans le chloroforme; ensuite la solution, diluée une fois avec le benzène, est passée à travers une colonne chromatographique d'alumine activée. La densité optique de l'éluat, renfermant le complexe du chrome seulement, est mesurée à 410 ou 425 mμ, en comparant avec le solvant. L'aluminium, le vanadium et le cobalt gênent lorsqu'on utilise la 8-hydroxyquinoléine comme réactif, mais ils ne gènent pas lorsqu'on utilise la 8-hydroxyquinaldine.

ZUSAMMENFASSUNG

Eine neue Methode zur Bestimmung von Chrom wird beschrieben. In einer geeigneten Lösung kann das dreiwertige Chrom in Gegenwart von dreiwertigem Eisen als 8-Oxychinolat oder 8-Oxychinaldat gefällt werden. Der getrocknete Niederschlag wird in Chloroform gelöst, die erhaltene Lösung einmal mit Benzol verdünnt und an aktiviertem Aluminiumoxyd chromatographiert. Die optische Dichte des Eluates, welches nur den Chromkomplex enthält, wird bei 410 oder 425 mμ im Vergleich zum Lösungsmittel gemessen. Aluminium, Vanadin und Kobalt stören wenn 8-Oxychinolin als Reagenz verwendet wird; bei Gebrauch von 8-Oxychinaldin ist die Methode eindeutig.

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SUR LA RÉACTION COLORIMÉTRIQUE DE L'ALUMINIUM AVEC LA QUINALIZARINE

par

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Un travail de revision des principales techniques colorimétriques de l'aluminium, effectué sous les auspices de la Commission Internationale de Chimie Analytique de l'Union Internationale de Chimie Pure et Appliquée, nous a conduits à l'étude de la réaction entre l'aluminium et la quinalizarine.

PARTIE EXPÉRIMENTALE

Appareils et solutions: Pour les mesures spectrophotométriques, on utilise un spectrophotomètre Beckman modèle DU et pour les mesures de pH un appareil Beckman avec électrode de verre.

La solution étalon d'aluminium contient 112 mg d'aluminium dans 1 litre (dosé gravimétriquement), sous forme de chlorure d'aluminium; on prépare ensuite diverses solutions de concentration connue, par dilution.

Réactif: Jusqu'à présent, on employait des solutions alcooliques saturées de réactif; pour nos mesures, il nous a paru plus avantageux de préparer des solutions alcalines, permettant d'obtenir des concentrations plus grandes et constantes. On prépare les solutions de 1,2,5,8-tétrahydroxyanthraquinone en dissolvant 0.100 g dans 100 ml de NaOH $0.1N$ (exempt de Al). Les solutions ainsi préparées sont assez stables.

Solution tampon: On la prépare en ajoutant 10 volumes d'acide acétique $5N$ à 9 volumes d'ammoniaque $5N$. On obtient un pH compris entre 5.4 et 5.9.

Formation du composé coloré

Selon la méthode de KOLTHOFF[1] à pH compris entre 5.4 et 5.8, l'aluminium forme une laque bleu violet avec une solution alcoolique de quinalizarine. La coloration apparaît après 15 minutes à froid ou en chauffant à 50° C.

Nous nous basons sur nos résultats expérimentaux pour apporter à la méthode précédente quelques modifications.

1) Formation du composé coloré, en employant une solution alcaline du réactif, la réaction est alors très rapide même à froid.

2) Emploi d'une solution très diluée de gélatine comme stabilisateur du composé formé, on obtient ainsi une solution transparente et stable pendant 12 heures.

3) Lorsqu'on a obtenu le composé coloré, on ajoute la solution tampon acide acétique-ammoniaque (pH de 5.9), l'excès du sel de sodium de la quinalizarine se transforme en quinalizarine libre légèrement jaune, tandis que la laque est parfaitement stable.

On a prouvé que le pH optimum pour la formation de la laque est celui que Kolthoff a fixé.

Courbes d'absorption du réactif et du composé coloré

Dans la région du spectre visible les courbes de densités optiques en fonction de la longueur d'onde du réactif et du composé coloré sont représentées sur la Fig. 1. La quinalizarine, au pH 5.8, présente un maximum d'absorption à 460 mμ, et au pH 10.5, deux maxima proches à 550 et 580 mμ. Pour le composé qui se forme entre l'aluminium et la quinalizarine on obtient un maximum d'absorption à 535 mμ. Comme on peut le voir sur les courbes de longueur d'onde au maximum d'absorption du composé coloré, la quinalizarine présente encore une absorption considérable.

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* présenté au XLVe Congrès International de Chimie Pure et Appliquée, Zurich, 1955.

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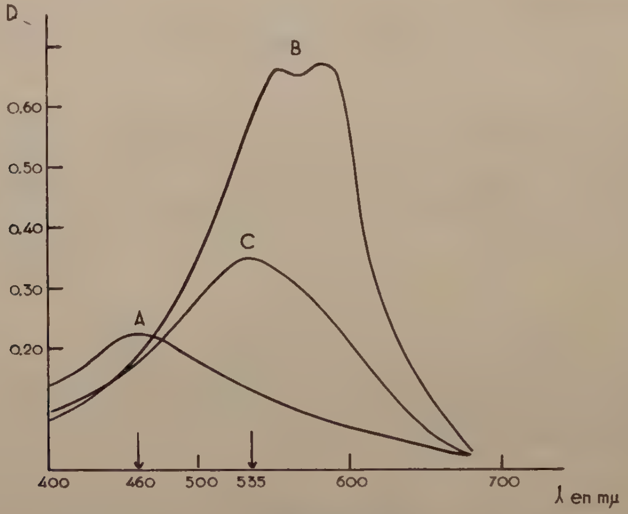

Fig. 1.

Courbe A: Spectre d'absorption de 0.3 ml de quinalizarine 0.1% dilués à 25 ml, pH = 5.8.
Courbe B: Spectre d'absorption de 0.3 ml de quinalizarine 0.1%, en solution alcaline, dilués à 25 ml, pH = 10.5.
Courbe C: Spectre d'absorption de 5 ml de sol. d'aluminium $4.14 \cdot 10^{-4} M$ et 0.3 ml de quinalizarine 0.1% dilués à 25 ml.

Etude spectrophotométrique du composé coloré

On étudie l'influence de la concentration du réactif sur l'intensité de la coloration. En prenant des quantités fixes d'aluminium et variables de quinalizarine, l'absorption augmente jusqu'à formation totale de la laque, puis se maintient constante, parallèle à la droite représentant l'absorption de la quinalizarine seule. Si on répète ces mesures pour une autre quantité constante d'aluminium on trouve le même type de courbe (Fig. 2).

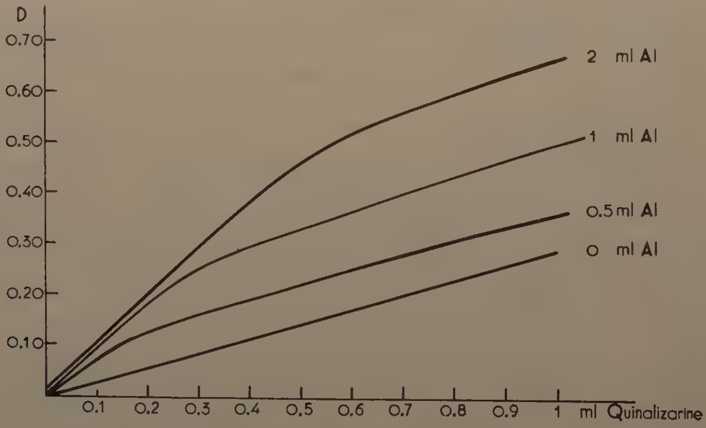

Fig. 2

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Le fait qu'un changement brusque de la pente de la courbe ne se produit pas indique que le composé est fortement dissocié en solution. Cela nous a fait supposer que l'aluminium et la quinalizarine forment un complexe de composition définie et non un composé d'adsorption comme mentionné jusqu'à présent dans la littérature. Mais le fait que ces composés se forment à des pH supérieurs aux pH de formation des hydroxydes correspondants, et que ces colorants polyhydroxyanthraquinoniques sont les plus adsorbés, appuie la théorie du composé d'adsorption. Cependant, cette adsorption du colorant sur la surface de l'oxyde hydraté peut être considérée comme un premier état qui, dans quelques cas, peut évoluer vers la formation d'un complexe interne.

La méthode de la relation molaire n'ayant pas donné des résultats sûrs, on a utilisé la méthode des variations continues proposée par JOB[2] et développée par VOSBURG ET COOPER[3] pour déterminer la proportion dans laquelle l'aluminium et la quinalizarine réagissent.

Nous représentons dans un graphique, à une longueur d'onde déterminée, les densités optiques des mélanges obtenus en fonction de x litres de réactif et nous obtenons une courbe qui passe par un maximum. Comme l'extinction molaire du réactif à la longueur d'onde employée (535 mμ) n'est pas nulle nous obtenons une seconde courbe pour les densités optiques de la quinalizarine seule (voir Fig. 3).

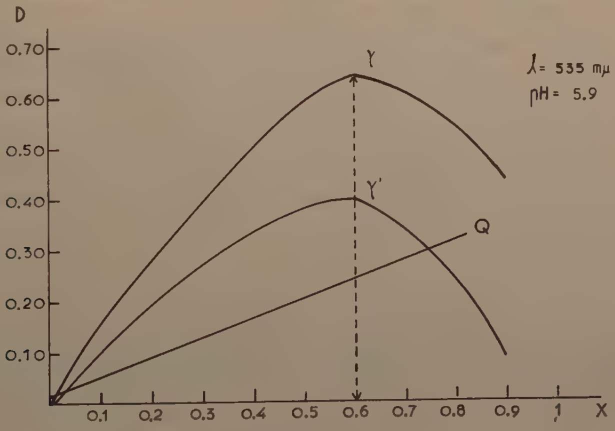

Fig. 3. x litres de solution de réactif $4.14 \cdot 10^{-4} M$ ajoutés à $1-x$ litres de solution d'aluminium $4.14 \cdot 10^{-4} M$.

La valeur de x dans laquelle la fonction y passe par un maximum nous donnera la valeur de n dans la formule du complexe Al(Quin.)$_n$ selon la relation $n = \frac{x}{1-x}$. Dans la Fig. 3 on peut observer que le maximum se trouve à 0.60 et par conséquent n sera 1.50.

Cette position du maximum se maintient lorsqu'on augmente les concentrations molaires des solutions d'aluminium et de quinalizarine, comme on peut le voir dans la Fig. 4.

En changeant légèrement les longueurs d'onde auxquelles on effectue les mesures, le maximum de la courbe correspond toujours à la relation molaire obtenue ci-dessus, ce qui démontre qu'il ne se forme qu'un seul composé (Fig. 5).

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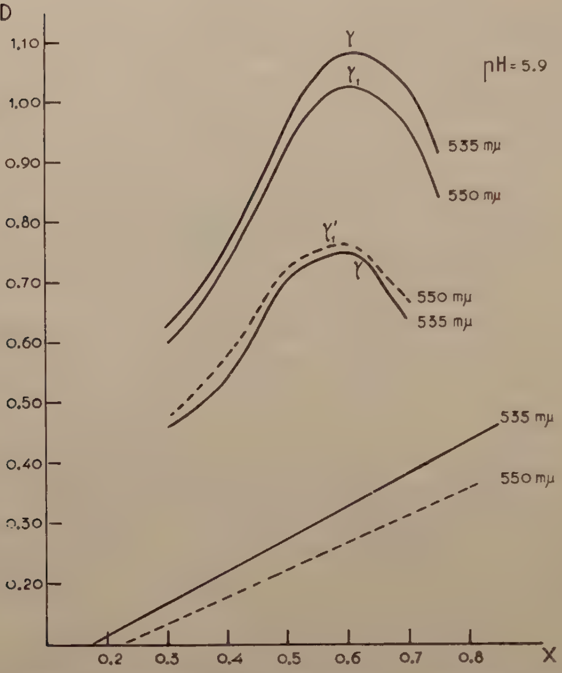

Fig. 4. x litres de solution de réactif $8.28 \cdot 10^{-4} M$ ajoutés à $1\text{-}x$ litres de solution d'aluminium $8.28 \cdot 10^{-4} M$.

Ceci nous a permis de supposer que l'aluminium et la quinalizarine réagissent dans la proportion 2:3 et le composé qui se forme aura la formule $Al_2(C_{14}H_8O_6)_3$. Il faudrait évidemment utiliser encore d'autres méthodes pour pouvoir établir a structure de ce complexe.

CONCLUSIONS

Cette étude a prouvé qu'on obtient une plus grande sensibilité en employant le réactif en solution alcaline, il en résulte une concentration définie et constante.

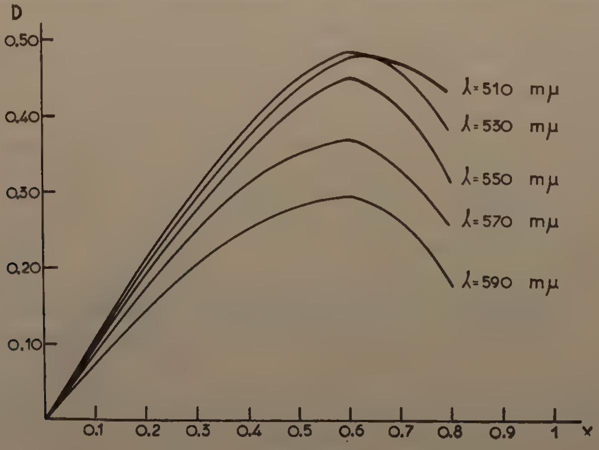

Fig. 5

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On obtient également une plus grande stabilité du composé formé en utilisant de la gélatine pour faciliter la dispersion colloïdale.

Le spectre d'absorption de la quinalizarine, à pH 4.9, présente un maximum à 460 mμ, tandis que dans un milieu alcalin, à pH 10.5, il y a deux maximums à 550 mμ et 580 mμ. Le complexe aluminium-quinalizarine présente un maximum à 535 mμ.

L'application de la méthode des variations continues nous a permis d'arriver à la conclusion qu'il se forme un composé dans la proportion 2:3.

La quinalizarine présente relativement peu d'intérêt pour le dosage de l'aluminium; il existe d'autres méthodes beaucoup plus avantageuses.

RÉSUMÉ

Nous avons étudié la réaction colorimétrique entre l'aluminium et la quinalizarine et, comme conclusion de nos observations, nous apportons quelques modifications dans les méthodes analytiques utilisées jusqu'à présent.

Nous avons étudié les courbes d'absorption du composé coloré et de la quinalizarine à différents pH. Nous appliquons la méthode des variations continues pour déterminer la composition du produit de réaction. De ces mesures spectrophotométriques, on peut déduire que les constituants forment un composé défini dans la proportion 2:3.

SUMMARY

The reaction between aluminium and quinalizarin has been studied, and some modifications have been made to the analytical procedure usually followed.

The absorption curve of the Al-quinalizarin compound and that of quinalizarin alone have been drawn. We applied the continuous variations method in order to determine the structure and composition of the reaction product. The spectrophotometric readings have shown that the constituents of the coloured compound are bound in a definite ratio, 2:3.

ZUSAMMENFASSUNG

Auf Grund einer Untersuchung der Reaktion zwischen Aluminium und Chinalizarin wurden einige Änderungen der üblichen analytischen Methoden vorgeschlagen.

Die Absorptionskurven von Chinalizarin und der gefärbten Al-Chinalizarin-Verbindung wurden aufgezeichnet. Um die Zusammensetzung der Al-Chinalizarin-Verbindung zu ermitteln, wurde die Methode der „kontinuierlichen Variationen" angewendet. Aus den Ergebnissen der photometrischen Messungen wurde geschlossen, dass die gefärbte Verbindung die Komponenten im Verhältnis 2:3 enthält.

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A PRECISE DIRECT HETEROMETRIC DETERMINATION OF TRACES OF COPPER WITH DIETHYLDITHIOCARBAMATE IN EXCESSES OF METALS

by

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INTRODUCTION

The determination of traces of copper with diethyldithiocarbamate (= CBM) has been studied extensively in recent years and there are numerous publications on this subject[1]. These studies were mostly concerned with the determination of copper in water, milk, other food stuffs and biological materials. Special attention was given to the determination of copper in excess of ferric iron. It was the purpose of the investigation to find the necessary conditions for a precise heterometric determination of copper with CBM. In previous investigations the reaction between mercury and CBM was studied by the authors[2]. As the material presented in this paper shows, the heterometric determination could be carried out very successfully in the suitable milieu with the presence of complexing agents. The reaction concerned is approximately of the same sensitivity as the reaction between cobalt and α-nitroso β-naphthol; 0.1–0.3 mg copper in 20 ml solution can be determined. Working conditions are presented which enable the heterometric determination of copper to be carried out in 7–10 minutes. The precision achieved was so great that in almost all cases theoretical values for copper were obtained without dependence on the amount of copper present. Generally, the copper made up only 0.1–0.2% of the total metal content. The determination of 0.06% of copper in iron presented no difficulties whatsoever. Compared with the heterometric titration of cobalt with α-nitroso β-naphthol[3] the reactions between copper and CBM required only *one third* of the time for a complete titration.

All the above advantages place the presented method in a position of primary importance and make its application universal for the direct heterometric determination of copper in metals, etc.

EXPERIMENTAL

Apparatus. A "Heterometer", designed by the first author, was used[4]. The light passed vertically through a cylindrical absorption cell of 4 cm diameter (in the experiments described in this paper) onto the photoelectric cell. The readings on the galvanometer were made with an accuracy of ± 0.001 microampere. They were recorded after increments of 0.1-0.2 ml of titrant were added, only when a constant value had been obtained, usually after a few seconds. The constancy of stirring of the solution was electronically controlled. The titrant was added from a 5 ml microburette (0.01 ml) the tip of which was dipped in the solution being analysed.

Temperature. All heterometric titrations were thermostatically controlled and were carried out at 20° C. A controlled temperature is generally unnecessary as the accuracy of the determination is independent of the temperature in the limits of ordinary room temperatures. Only the absolute *values* of the optical density are influenced by the temperature; these are more constant and more easily controlled when experiments, carried out at different times and at a constant temperature, are compared.

Stirring. The rate of stirring of the solution was generally the maximum consistent with stable measurements.

Readings. Readings of the galvanometer were constant in a few seconds in the presence of the supplementary neutral electrolyte (NH_4NO_3). This was just as fast as in a regular homogeneous titration.

Reproducibility. On repeating titrations at different times it was found that the maximum optical density values obtained did not change by more than one unit in the second decimal place.

Volume. The volume analysed was, in all cases, 20 ml (aqueous solution), containing 0.19 mg-0.254 mg of copper. The molarity of the copper in the analysed solution was, therefore, $5 \cdot 10^{-5}$-$6.7 \cdot 10^{-5} M$ or 1 part copper per 100,000 parts of solution.

Reagent. The sodium diethyldithiocarbamate (= CBM) was an Eastman Kodak reagent. Diluted CBM solutions were often prepared from a stock solution which was stored in a dark brown bottle. The stock solution was stable for months. All other chemicals used, were either analytical reagents or chemically pure reagents.

RESULTS

General aspects

Accuracy. Almost all of the titrations presented were carried out with the highest accuracy and the determinations of copper were made with an error equal to zero. In spite of this a titration lasted only 7-10 minutes.

In the following tables and figures a selection of results obtained in the heterometric study of the reaction between copper and carbamate (= CBM), are presented. The numeration is the same in the tables and in the figures. The copper can be precipitated from acidic, neutral or alkaline solutions and the pH of the solution is probably not of primary importance. The presence of neutral electrolytes in a sufficient concentration is of greater importance for the heterometric titration. This factor determines whether precipitation occurs at all, and whether the precipitate can be used, for a quick an precise determination of copper. A further problem is the kind of complexing agents and their concentration which could be used without interfering with the heterometric precipitation of copper.

Table I and Fig. 1 present some results obtained in the *absence* of foreign metals on changing the composition and the concentration of the electrolytes in the solution. As was ascertained the *ammoniacal citrate solution was the most favorable for the heterometric titrations.* In the presence of *ammonium nitrate* the titration proceeded very quickly, and the *first* maximum optical density point was determined easily and with precision. *In the presence of citrate a horizontal maximum line* was obtained immediately after the first maximum point. In the absence of citrate the densities generally dropped after the first maximum. From previous studies[5] on the composition and the structure of citrate complexes we know that these are mostly stable in the alkaline solution. No other complexing agents could compete with citrate in these heterometric titrations. A large number of experiments were carried out by us with *ethylenediaminetetraacetate* (= EDTA) in an alkaline medium both in the presence and in the absence of excesses of foreign metals. Although the end-point of the titration could be fixed in many cases, the results were not sufficiently sure, smooth curves were not obtained and the titration generally lasted a longer time.

TABLE I

Composition: 3 ml *a* M $Cu(NO_3)_2$ + K ml supplements + (17-K) ml H_2O + x ml 0.0028M CBM. T = 20° C. Content Cu 0.190 mg, 0.254 mg, 0.381 mg.

Expt. number	Molarity of $Cu(NO_3)_2$ (a)	Supplements		Found					
				ml CBM (x)	Maximum density value	Initial prepn. ml	Titration time (min)	Theoretical point ml	Error %
1	0.00133	2 ml 2M NH_3		3.00	0.51**	0.1	45	3.00	0.0
2	0.00133	4 ,, M CH_3COONa			0.29****		20		
3	0.00133	2 ,, 2M NH_3 + 4 ml M NH_4NO_3		3.00	0.57**	0.1	10	3.00	0.0
4	0.002	2 ,, 2M ,, + 2 ,, ,, ,,		4.54	0.77	0.1	15	4.5	0.9
5	0.001	2 ,, 2M ,, + 2 ,, ,, ,,		2.20	0.50**	0.1	15	2.25	−2.2
6	0.002	2 ,, 2M ,, + 5 ,, ,, ,,		4.50	1.00	0.1	10	4.5	0.0
7	0.001	2 ,, 2M ,, + 5 ,, ,, ,,		2.25	0.34**	0.1	20	2.25	0.0
8	0.001	2 ,, 2M ,, + 2 ,, ,, ,,	+ 3 ml M Na_3-citrate	2.30	0.45**	0.1	20	2.25	2.2
9	0.00133	2 ,, 2M ,, + 4 ,, ,, ,,	+ 3 ,, ,, ,,	3.00	0.51*	0.1	10	3.00	0.0
10	0.00133	1 ,, conc. ,, + 4 ,, ,, ,,	+ 3 ,, ,, ,,	3.00	0.48*	0.1	10	3.00	0.0
11	0.002	2 ,, 2M ,, + 4 ,, ,, ,,	+ 3 ,, ,, ,,	4.50	0.60*	0.1	8	4.50	0.0
12	0.00133	1 ,, conc. —	+ 9 ,, ,, ,,	3.00	0.40*	0.1	10	3.00	0.0
13	0.00133	2 ,, 2M ,, + 4 ml M NH_4NO_3	+ 5 ,, ,, ,,	3.00	0.35*	0.1	10	3.00	0.0
14	0.001	2 ,, 2 ,, ,, + 5 ,, ,, ,,	+ 3 ,, ,, ,,	2.33	0.45**	0.1	10	2.25	3.5
15	0.00133	2 ,, 2 ,, ,, + 4 ,, ,, ,,	+ 3 ,, ,, K_2-tartrate	3.00	0.48	0.1	10	3.00	0.0
16	0.001	1 ,, conc. ,, + 4 ,, ,, ,,	+ 3 ,, ,, ,,	2.27	0.51**	0.1	10	2.25	0.9
17	0.001	2 ,, 2M ,, + 5 ,, ,, ,,	+ 8 ,, 0.125M $Na_4P_2O_7$	2.30	0.44**	0.1	15	2.25	2.2
18	0.00133	1 ,, conc. ,, + 4 ,, ,, ,,	+ 11 ,, 0.125M ,,	3.00	0.44*	0.1	10	3.00	0.0
19	0.00133	1 ,, ,, ,, + 4 ,, ,, ,,	+ 10 ,, 0.2M Na_4-EDTA	3.00	0.58***	1.6	20	3.00	0.0
19a	0.00133	2 ,, 2M ,, + 4 ,, ,, ,,	+ 5 ,, 0.1M ,,	3.00	0.62***	0.1	22	3.00	0.0

CBM = Sodium diethyldithiocarbamate; EDTA = Ethylenediaminetetraacetate;

* after the maximum a horizontal density line;
** after the maximum density decreases;
*** no smooth titration curve;
**** fluctuation.

TABLE II

Composition: 3 ml 0.0013*M* $Cu(NO_3)_2$ + *K* ml supplements + (17-*K*) ml H_2O + *x* ml 0 0028*M* CBM. T = 20° C. Content Cu 0.254 mg (0.38 mg).

Expt. number	*Supplements*	*Cu %*	*Found*		
			ml CBM (x)	*Maximum density value ***	*Error %*
20	2 ml 2*M* NH_3 + 4 ml *M* NH_4NO_3 + 2 ml *M* $Ca(NO_3)_2$	0.31	3.00	0.51	0.0
21	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 2 ,, ,, $SrCl_2$	0.14	,,	0.52	,,
22	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 2 ,, ,, $BaCl_2$	0.09	,,	0.50	,,
23	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 2 ,, ,, $MgCl_2$	0.52	,,	0.48	,,
24	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 11 ,, 2*M* ,,	0.04	,,	0.35	,,
25	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, *M* Na_3-citrate + 2 ml *M* $Zn(NO_3)_2$	0.19	,,	0.42	,,
26	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, ,, $NiCl_2$	0.21	,,	0.39	,,
27	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, ,, $CoCl_2$	0.21	,,	0.25	,,
*28	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, ,, ,,	0.32	4.50	0.35	,,
29	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, ,, $MnCl_2$		∞	0.7	,,
30	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, ,, $CdCl_2$	0.10	3.00	0.44	,,
31	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, ,, $Pb(NO_3)_2$	0.06	,,	0.58	,,
32	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 8 ,, 0.1*M* $TlNO_3$	0.15	,,	0.69	,,
33	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 10 ,, 0.1*M* $AgNO_3$		∞	0.0	,,
34	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, *M* $AlCl_3$	0.46	3.00	0.55	,,
35	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 5 ,, ,, ,, + 4 ,, ,, ,,	0.23	,,	0.33	,,
36	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, 0.1*M* $Cr(NO_3)_3$	2.4	,,	0.50	,,
37	1 ,, conc. ,, + 4 ,, ,, ,, + 5 ,, ,, ,, + 4 ,, *M* $FeCl_3$	0.11	,,	0.45	,,
38	1 ,, ,, ,, — + 9 ,, ,, ,, + 6 ,, *M* ,,	0.075	,,	0.33	,,
39	1 ,, ,, ,, + 4 ml *M* NH_4NO_3 + 3 ,, ,, ,, + 2 ,, 0.1*M* $SbCl_3$	1.03	,,	0.48	,,
40	2 ,, 2*M* ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 5 ,, 0.1 ,, $Ce(NO_3)_3$	0.36	,,	0.50	,,
41	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 8 ,, 0.1 ,, $La(NO_3)_3$	0.23	,,	0.54	,,
42	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, ,, ,, + 2 ,, *M* $ZrO(NO_3)_2$	0.17	,,	0.48	,,
43	2 ,, 2 ,, ,, + 4 ,, ,, ,, — + 1 ,, ,, Na_2MoO_4	0.26	,,	0.64	,,
44	2 ,, 2 ,, ,, + 4 ,, ,, ,, + 3 ,, *M* Na_3-citrate + 2 ,, 0.1*M* $Th(NO_3)_4$	0.54	,,	0.64	,,

CBM = Sodium diethyldithiocarbamate; initial precipitation throughout at 0.1 ml CBM; titration time 7-10 minutes;

* 3 ml 0.002*M* $Cu(NO_3)_2$;
** horizontal maximum line in all experiments;
∞ no end-point.

Tartrate in alkaline solution could in no way compete with the citrate: in the former case a precipitate usually appeared in the presence of foreign metals *before* the carbamate was added. Titrations with carbamate could only be carried out when the concentration of the foreign metal was low.

In spite of this there are many special cases in which tartrate could be used more successfully than citrate (*e.g.* Sb).

The use of *pyrophosphate* evidently gave no better results. Furthermore, the solubility of sodium pyrophosphate is many times lower than that of trisodiumcitrate or tartrate.

Table II and Figs. 2 and 3 present results obtained in the presence of excesses of foreign metals in alkaline citrate solutions. Table III and Fig. 4 likewise show these results in the presence of tartrate.

The results presented in this work are of interest for many reasons. Firstly, the amount of the foreign metals which may be present in solution, without any influence on the titration of copper, is very high. This concerns metals which could not be satisfactorily detected by direct methods or for the detection of which no direct methods exist. Secondly, the copper could be determined in almost all cases *with an error which is equal to zero.* In spite of this, the heterometric titrations of copper with carbamate required no more

TABLE III

Composition: 3 ml *a* *M* $Cu(NO_3)_2$ + 4 ml *M* NH_4NO_3 + 3 ml *M* K_2-tartrate + *K* ml supplements + (10-*K*) ml H_2O + *x* ml *b* *M* CBM. T = 20° C.
Content Cu 0.254 mg, 0.127 mg.

Expt. number	*Molarity of*		*Supplements*	*Cu %*	*Found*			
	Cu(NO₃)₂ (a)	*CBM (b)*			*ml CBM (x)*	*Maximum density value*	*Titration time min*	*Error %*
45	0.00133	0.0028	2 ml 2*M* NH_3 + 2 ml *M* $AlCl_3$	0.46	3.00	$0.52^{1)}$	10	0.0
46	0.00133	0.0028	1 ,, conc. ,, + 6 ,, 0.1*M* $SbCl_3$	0.35	3.00	$0.62^{1)}$	10	,,
47	0.00133	0.0028	1 ,, ,, ,, + 9 ,, 0.1 ,, ,,	0.23	3.00	$0.88^{1)}$	10	,,
48	0.00066	0.0014	1 ,, ,, ,, + 9 ,, 0.1 ,, ,,	0.11	3.00	$0.40^{2)}$	15	,,
49	0.00133	0.0028	2 ,, 2*M* ,, + 8 ,, 0.1 ,, $Th(NO_3)_4$	0.13	3.00	$0.65^{1)}$	10	,,
50	0.00133	0.0028	2 ,, 2 ,, ,, + 8 ,, 0.1 ,, $VOSO_4$	0.61	3.00	$0.55^{1)}$	10	,,
51	0.00133	0.0028	2 ,, 2 ,, ,, + 8 ,, 0.1 ,, Na_2MoO_4	0.33	3.00	$0.60^{2)}$	10	,,
52	0.00133	0.0028	2 ,, 2 ,, ,, + 4 ,, 0.2 ,, $ZrO(NO_3)_2$	0.35	3.00	$0.44^{1)}$	10	,,
53	0.00133	0.0028	1 ,, conc. NH_3 + 8 ,, *M* K_2-tartrate + 6ml *M* $AlCl_3$	0.16	3.00	$0.35^{1)}$	9	,,

CBM = Sodium diethyldithiocarbamate; 1) after the maximum a horizontal density line;
2) after the maximum, the density decreases. Initial precipitation always at 0.1 ml CBM.

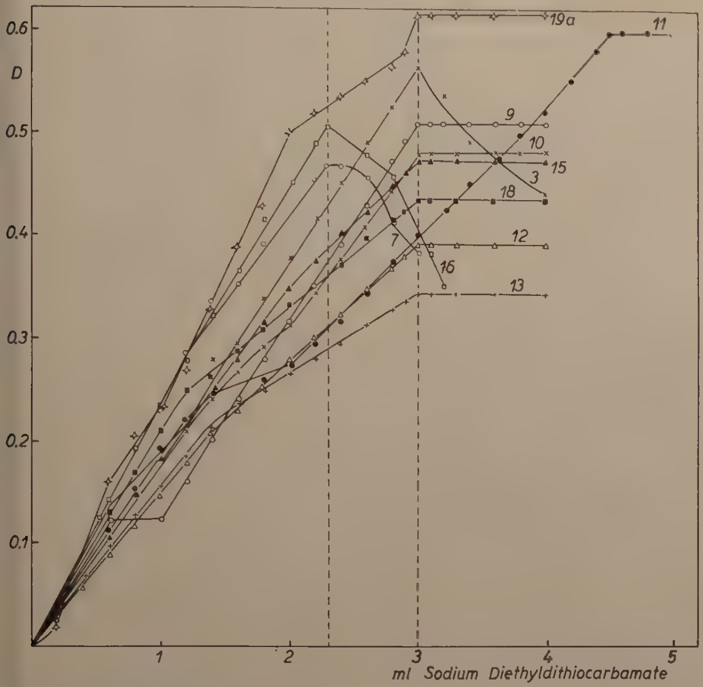

Fig. 1. Titrations of copper in the presence of complexing agents.

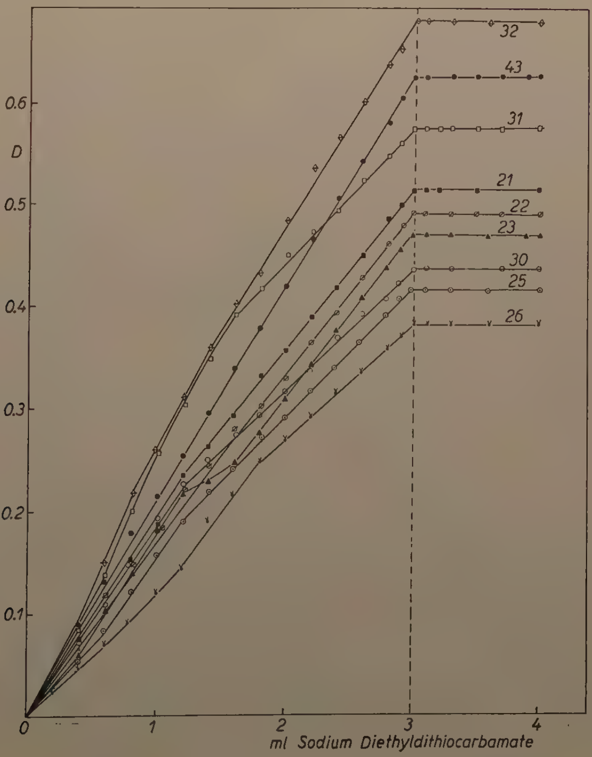

Fig. 2. Titrations of copper in citrate solution in the presence of excesses of foreign metals.

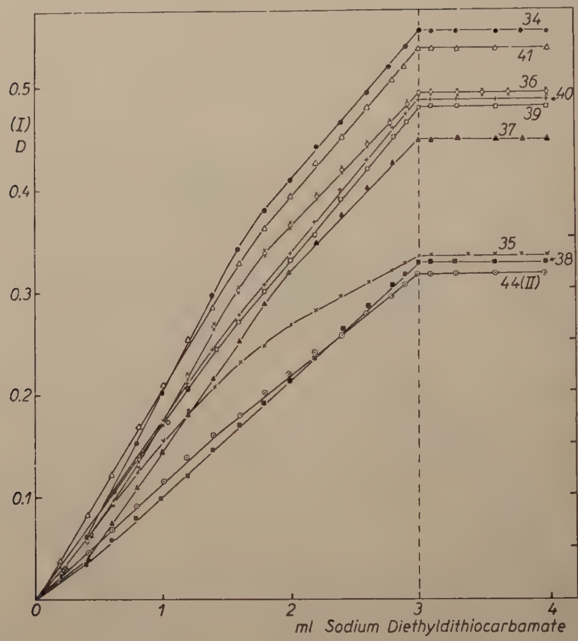

Fig. 3. Titrations of copper in citrate solution in the presence of excesses of polyvalent cations.

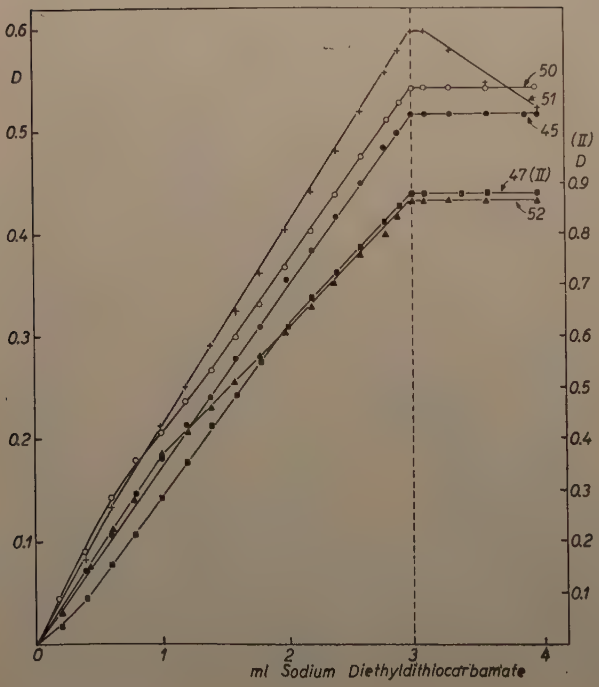

Fig. 4. Titrations of copper in tartrate solution in the presence of excesses of foreign metals.

than 7 to 10 minutes. The following calculation demonstrates the sensitivity and the precision of the direct heterometric determination of traces of copper with CBM in the presence of $\gtrsim$ 99.8% other metals.

In analysing 0.2 mg copper in 20 ml solution, 1 part of copper in 100,000 parts of solution is determined. Since the titrant is added in increments of 0.1 ml and the copper is determined with a zero error (using 3 ml CBM for a full titration) an amount of copper which is 30 times less than that contained in the analysed solution can be safely determined. This means that 1 part of copper in 3,000,000 parts of solution can be determined with an error equal to zero.

Titrations in the presence of neutral supplements and complexing agents

In the presence of *sodium acetate* (expt. 2) the titration was unsafe because the readings fluctuated. A satisfactory end-point could not be obtained. When the titration was carried out in the presence of an *excess of ammonia* but in the *absence* of ammonium nitrate (expt. 1) the titration lasted about *five times* as long as in the presence of the latter. Apart from this, the maximum density values and the precision were the same in both cases. It is likely that the favorable action of *ammonium nitrate* was caused by its presence as a concentrated neutral electrolyte. A sufficient amount of ammonium nitrate was therefore added to all solutions to be analysed. In the very *dilute* solutions of copper, excesses of ammonium nitrate seemed to decrease the maximum density value somewhat (expts. 5 and 7). Even in the presence of sodium citrate no horizontal maximum density line was obtained and the density values dropped after the maximum point.

In general the addition of excesses of *trisodium citrate* to the analysed copper solutions was favorable for the titration. Smooth titration curves were obtained in all cases. The precise location of the *first* maximum density point was very simple because a *horizontal density line* was obtained immediately after the first maximum point (expts. 9-13). If, however, too great an excess of titrant was added the density values began to decrease again.

To a certain extent, tartrate, pyrophosphate, tripolyphosphate and ethylenediaminetetraacetate (= EDTA) could be used as complexing agents (expts. 15 and 18). In the presence of EDTA in ammoniacal solution the end-point of the titration was located but the curves were not smooth and the titration time was longer than usual (expts. 19 and 19a). Summarizing, it may be said that *the titration of copper proceeded quickly and safely when an ammoniacal solution was used, containing excesses both of ammonium nitrate and of sodium citrate.*

Titrations in the presence of excesses of foreign metals

In the presence of Ca, Sr, Ba and Mg. No complexing agents whatever were necessary (expts. 20-23). The influence on the maximum density value of the blank was not appreciable. Probably the salts could have been present in much higher concentrations. In all cases the percentage of copper was 0.15-0.3%. At the higher concentration of magnesium the maximum value decreased (expt. 24) and in this case the use of a somewhat higher amount of copper would have been preferable.

In the presence of Zn^{+2} and Cd^{+2}. The determination was carried out most successfully with trisodium citrate in a mole per mole amount at least equal to the foreign metal (expts. 25 and 30). Probably the concentration of the foreign metals could have been higher than that used. The copper made up 0.1-0.2% of the total metal content. Tartrate was also used as a complexing agent, but because of the insolubility of the tartrates the content of the foreign metal had to be lower.

In the presence of Mn^{+2}. In the presence of ammoniacal citrate, the density rose continuously after the calculated end-point had been reached (expt. 29). The same experiment, when carried out in an excess of ammoniacal ethylenediaminetetraacetate, (= EDTA) gave a clear end-point at the calculated point but no smooth titration curve was obtained.

In the presence of Co^{+2} *and* Ni^{+2}. Sodium citrate was used as complexing agent, (expts. 26-28). The copper made up 0.2-0.3% of the total metal content. The maximum density value was considerably lower in the presence of cobalt.

In the presence of Pb^{+2}. The citrate solution must be strongly ammoniacal and an excess of citrate must be present (the soluble complexes of lead citrate are discussed elsewhere[6]). The copper amounted to 0.06% of the total metal content (expt. 31). The maximum density obtained was high.

In the presence of Al^{+3}. The determination was carried out either in ammoniacal citrate or tartrate solutions. In both cases a molar excess of the complexing agent, calculated on the amount of aluminium present, must be added (expts. 34, 35, 45 and 53). In expt. 53, in the presence of excesses of tartrate, the copper content was as low as 0.16%.

In the presence of Cr^{+3}. In the presence of citrate the amount of chromium had to be very low, otherwise precipitation occurred before the addition of titrant. More chromium was present in tartrate solution. The densities in the latter cases were very low. In the citrate solution the copper amounted to 2.4% (expt. 36).

In the presence of Fe^{+3}. A highly concentrated ammoniacal solution was used (expts. 37 and 38). The determination was best made in excesses of citrate. The copper amounted to 0.075%. Theoretical results were always obtained, but in the presence of a highly concentrated citrate solution the maximum density value was depressed. In excesses of tartrate, the amount of iron which could be present in solution was less than with citrate.

In the presence of Tl^{+}. The maximum concentration of Tl^{+} in the citrate solutions was less than 0.05*M* (expt. 32). The maximum density value obtained was very high (expt. 32). With tartrate, a precipitate was obtained before titrant was added.

In the presence of Ag^{+}. Neither in citrate or tartrate nor in EDTA solutions did copper precipitate when the solution contained silver (expt. 33).

In excesses of Sb^{+3}. The amount of Sb^{+3} which could be in the ammoniacal citrate solution was very low ($\lessdot$0.01*M*). When not low, precipitation occurred before the titration (expt. 39). In this case, the copper amounted to 1%. In contrast to this the tartrate solution contained *five* times more antimony (expts. 46-48) and the copper content was reduced to 0.23%. In expt. 48 the copper content was only 0.11%. It was interesting that in the presence of antimony the maximum density values of the copper carbamate were very high. This was evaluated in expt. 48 in which only 0.127 mg copper was used for the analysis.

In the presence of Ce^{+3} *and* La^{+3}. The amounts given in the table for these metals (expts. 40 and 41) are the highest that may be present in the citrate solution. The copper made up 0.2-0.4% of the metal content. The tartrates were insoluble and could not be titrated.

In the presence of ZrO^{+2}. In experiments 42 and 52 the highest amount of zirconium which could be held in the solution was used and the concentration was 0.05*M*. In the citrate solution the concentration of zirconium was equal to 0.1*M* and the copper made up 0.17% of the metal content. In the tartrate solution the zirconium was 0.05*M* and the copper amounted to 0.35%.

In the presence of Na_2MoO_4. The molybdate was at a molarity of 0.05*M* and the copper made up 0.26% (expt. 43).

In the presence of Th^{+4}. In the experiments 44 and 49 the highest amounts of Th^{+4} which could be held in solution were used. In the tartrate solution the copper content was reduced to 0.13%. The molarity of thorium nitrate was 0.01*M* (citrate) and 0.04 (tartrate).

ANALYSIS

General method: 20 ml of an aqueous solution (the composition of which is given below), containing 0.25-0.5 mg of copper, are titrated heterometrically with an aqueous solution of 0.0028*M* sodium diethyldithiocarbamate. The solution to be analysed may contain up to >99.5% of any foreign metal.

Titration time: 7-10 minutes. Error: mostly zero.

Composition: In addition to the metals, the solution to be analysed must contain the following supplements which are added in this order:

3 ml *M* Na_3-citrate + 2 ml 2*M* NH_4NO_3 + 0.5-1.0 ml conc. NH_3.

Remarks: If traces of copper have to be analysed in alloys, the molar amount of citrate (or tartrate) must exceed the molar amount of the sum of the other metals. If the copper content of aluminium is analysed, the use of potassium tartrate instead of citrate is preferable. The same is true of solutions which contain large excesses of antimony or thorium.

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SUMMARY

The most favorable conditions for the heterometric titration of copper with sodium diethyldithiocarbamate and the influence of complexing agents on the titration were investigated.

Titrations of copper were carried out in the presence of large excesses (> 99.5%) of most of the common cations. A method is presented for a precise determination of traces of copper in metals and salts.

The titration time was 7-10 minutes. In most titrations the amount of copper present was determined with an error close to zero.

RÉSUMÉ

Les auteurs ont étudié les conditions de dosage hétérométrique du cuivre avec le diéthyldithiocarbamate de sodium, ainsi que l'influence de réactifs complexants. Les titrages ont été effectués en présence de la plupart des cations ordinaires en excès (> 99.5%). Une méthode précise est proposée pour le dosage des traces de cuivre dans divers métaux et sels. La détermination s'effectue en 7 à 10 minutes. Des résultats théoriques ont été obtenus dans la plupart des dosages.

ZUSAMMENFASSUNG

Die Bedingungen, welche für die heterometrische Titration von Kupfer mit Natriumdiäthyldithiocarbamat am günstigsten sind, sowie der Einfluss der komplexbildenden Körper auf die Titration wurden untersucht. Titrationen von Kupfer in Gegenwart grosser Überschüsse der meisten üblichen Kationen (> 99.5%) wurden ausgeführt. Eine Methode zur genauen Bestimmung von Spuren von Kupfer in Metallen und Salzen wurde vorgeschlagen. Die Titrationsdauer betrug 7-10 Minuten. Die meisten Titrationen ergaben theoretische Werte.

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POTENTIOMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS

XXI. REDUCTION WITH FERROUS ETHYLENEDIAMINE SULPHATE

CERIC SULPHATE METHOD

by

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SINGH *et al.*[1] used ferrous ethylenediamine sulphate for the indirect volumetric determinations of potassium chlorate, potassium bromate, potassium metaperiodate, potassium dichromate, potassium ferricyanide, potassium permanganate, potassium persulphate, hydrogen peroxide and ceric sulphate. The excess of ferrous ethylenediamine sulphate added to each of the substances was titrated with standard potassium permanganate, standard potassium dichromate and standard ceric sulphate solution.

SINGH *et al.*[2] also used ferrous ethylenediamine sulphate to estimate indirectly potassium permanganate, ceric sulphate, potassium chlorate, hydrogen peroxide, potassium persulphate, potassium dichromate, and potassium bromate by a potentiometric method using standard potassium permanganate as the titrant. In the present investigation these substances have been determined indirectly using ferrous ethylenediamine sulphate solution as reducing agent. The excess of standard ferrous ethylenediamine sulphate solution added to each of the substances in acid medium was titrated potentiometrically with standard ceric sulphate solution.

EXPERIMENTAL

A known weight of each substance was mixed with an excess of standard ferrous ethylenediamine sulphate solution and the mixture acidified with sulphuric acid to keep its normality between 1 to 2*N*. In the case of potassium chlorate and potassium bromate the normality of the mixture with respect to the acid was kept between 4 and 6*N*. The mixture containing potassium chlorate was heated to 80° C for about ten minutes in an atmosphere of carbon dioxide and then allowed to cool. In each case the excess ferrous ethylenediamine sulphate solution was titrated at 20° C against standard ceric sulphate solution by a potentiometric method. The mixture was kept stirred by a mechanical stirrer during the titrations. A bright platinum foil immersed in the solution to be titrated was used as an oxidation-reduction electrode, and this was coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge. During the titration the progress of the reaction was studied potentiometrically. At the equivalence point a sharp jump in potential was observed in each titration.

A series of potentiometric titrations were performed with different amounts of each substance. One titration, as typical of the set, is recorded in Table I.

All chemicals, except ceric sulphate, used in this investigation were of guaranteed purity. Ceric sulphate was standardized with pure arsenious oxide[3].

References p. 572.

TABLE I

TITRATION OF 0.0221 g OF POTASSIUM PERMANGANATE MIXED WITH 25 ml OF WATER, 28.00 ml OF 0.05N FERROUS ETHYLENEDIAMINE SULPHATE AND 30 ml OF 4N H_2SO_4 AGAINST 0.05N CERIC SULPHATE SOLUTION

Ceric sulphate ml	*E.M.F. volts*	*E/C mV/ml*
0.00	0.2735	
		2
2.00	0.2780	
		2
5.00	0.2850	
		3
7.00	0.2905	
		3
9.00	0.2965	
		4
10.00	0.3000	
		4
11.00	0.3044	
		6
12.00	0.3099	
		8
13.00	0.3181	
		10
13.30	0.3211	
		12
13.50	0.3234	
		37
13.80	0.3344	
		230
14.00	0.3805	
		1354 (Maximum)
14.05	0.4482	
		1200
14.10	0.5082	
		591
14.20	0.5673	
		164
14.50	0.6166	
		67
15.00	0.6502	
		20
16.00	0.6698	
		9
17.00	0.6789	
		6
18.00	0.6851	
		5
19.00	0.6905	
		4
21.00	0.6989	
		3
23.00	0.7045	
		3
25.00	0.7104	
		2
28.00	0.7171	

The titrations, one for each substance, are represented by the curves, A to G, given in Fig. 1.

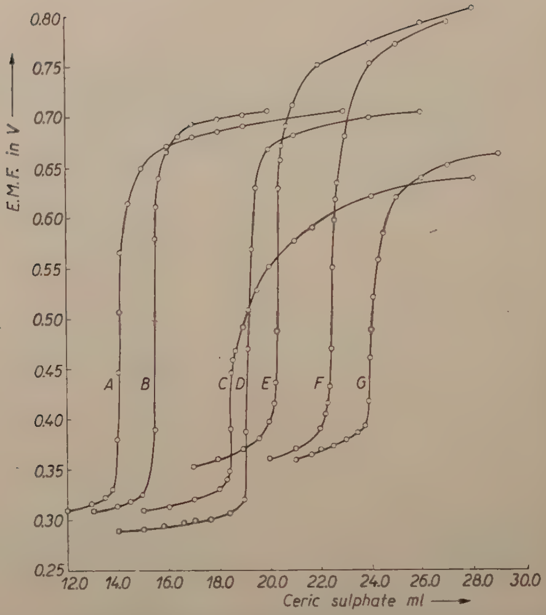

Fig. 1. Curves A $KMnO_4$
B $Ce(SO_4)_2$
C $KClO_3$
D H_2O_2
E $K_2S_2O_8$
F $K_2Cr_2O_7$
G $KBrO_3$

In these titrations it is evident that with the addition of the titrant the E.M.F. rose steadily till the equivalence point. At the equivalence point there was a sharp jump in potential followed by a steady rise in each case.

From the amount of ceric sulphate used, corresponding to the equivalence point in each titration, the amount of ferrous ethylenediamine sulphate required for the reduction of each substance was calculated and consequently the amount of each substance was determined. The results recorded in Tables II-VIII show that potassium permanganate, ceric sulphate, potassium chlorate, hydrogen peroxide, potassium persulphate, potassium dichromate and potassium bromate can be determined indirectly by the potentiometric method, using ferrous ethylenediamine sulphate (FES) as a reducing agent.

TABLE II

POTASSIUM PERMANGANATE

$KMnO_4$ taken g	*0.05N FES added ml*	*0.05N $Ce(SO_4)_2$ used for excess FES ml*	*0.05N FES used by $KMnO_4$ ml*	*$KMnO_4$ found g*
0.0120	16.00	8.33	7.67	0.0121
0.0151	20.00	10.38	9.62	0.0152
0.0221	28.00	14.04	13.96	0.0221
0.0344	44.00	22.18	21.82	0.0345
0.0398	50.00	24.83	25.17	0.0398

TABLE III

CERIC SULPHATE

$Ce(SO_4)_2$ taken g	*0.05N FES added ml*	*0.05N $Ce(SO_4)_2$ used for excess FES ml*	*0.05N FES used by $Ce(SO_4)_2$ ml*	*$Ce(SO_4)_2$ found g*
0.1199	15.00	7.78	7.22	0.1200
0.1671	20.00	9.93	10.07	0.1673
0.2221	26.00	12.63	13.37	0.2221
0.2734	32.00	15.53	16.47	0.2735
0.3141	38.00	19.08	18.92	0.3142

TABLE IV

POTASSIUM CHLORATE

$KClO_3$ taken g	0.05N FES added ml	0.05N $Ce(SO_4)_2$ used for excess FES ml	0.05N FES used by $KClO_3$ ml	$KClO_3$ found g
0.0069	14.00	7.13	6.87	0.0070
0.0132	26.00	13.23	12.77	0.0131
0.0164	32.00	15.98	16.02	0.0164
0.0201	38.00	18.46	19.54	0.0200
0.0213	42.00	20.98	21.02	0.0214

TABLE V

HYDROGEN PEROXIDE

H_2O_2 taken g	0.05N FES added ml	0.05N $Ce(SO_4)_2$ used for excess FES ml	0.05N FES used by H_2O_2 ml	H_2O_2 found g
0.0036	10.00	5.78	4.22	0.0036
0.0071	20.00	11.63	8.37	0.0071
0.0128	30.00	14.78	15.22	0.0129
0.0160	38.00	19.13	18.87	0.0160
0.0198	46.00	22.68	23.32	0.0198

TABLE VI

POTASSIUM PERSULPHATE

$K_2S_2O_8$ taken g	0.05N FES added ml	0.05N $Ce(SO_4)_2$ used for excess FES ml	0.05N FES used by $K_2S_2O_8$ ml	$K_2S_2O_8$ found g
0.0511	15.00	7.44	7.56	0.0511
0.0656	20.00	10.28	9.72	0.0657
0.0986	30.00	15.39	14.61	0.0987
0.1185	36.00	18.48	17.52	0.1184
0.1326	40.00	20.37	19.63	0.1327

TABLE VII

POTASSIUM DICHROMATE

$K_2Cr_2O_7$ taken g	0.05N FES added ml	0.05N $Ce(SO_4)_2$ used for excess FES ml	0.05N FES used by $K_2Cr_2O_7$ ml	$K_2Cr_2O_7$ found g
0.0107	10.00	5.58	4.42	0.0108
0.0263	20.00	9.24	10.76	0.0264
0.0412	32.00	15.17	16.83	0.0412
0.0443	38.00	19.88	18.12	0.0444
0.0526	44.00	22.48	21.52	0.0527

References p. 572.

TABLE VIII

POTASSIUM BROMATE

$KBrO_3$ taken g	0.05N FES added ml	0.05N $Ce(SO_4)_2$ used for excess FES ml	0.05N FES used by $KBrO_3$ ml	$KBrO_3$ found g
0.0068	10.00	5.08	4.92	0.0068
0.0112	16.00	7.83	8.17	0.0113
0.0177	26.00	13.17	12.83	0.0178
0.0260	38.00	19.24	18.76	0.0261
0.0335	48.00	23.93	24.07	0.0335

SUMMARY

Ferrous ethylenediamine sulphate has been used as a reducing agent to determine indirectly potassium permanganate, ceric sulphate, potassium chlorate, hydrogen peroxide, potassium persulphate, potassium dichromate and potassium bromate by a potentiometric method. An excess of ferrous ethylenediamine sulphate added to each of the substances in acid medium was titrated with a standard solution of ceric sulphate, using platinum foil as an oxidation-reduction electrode coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge.

RÉSUMÉ

Le sulfate double de fer(II) et d'éthylènediamine est proposé comme réducteur pour le dosage potentiométrique indirect du permanganate de potassium, du sulfate de cérium(IV), du peroxyde d'hydrogène, des persulfate, dichromate et bromate de potassium. L'excès de sulfate double de fer(II) et d'éthylènediamine ajouté à chacune de ces substances, en milieu acide, est titré au moyen d'une solution étalon de sulfate de cérium(IV); on utilise une feuille de platine comme électrode d'oxydo-réduction, reliée à une électrode au calomel saturée par un pont d'agar-agar-chlorure de potassium.

ZUSAMMENFASSUNG

Das Eisen(II)äthylendiaminsulfat wird als Reduktionsmittel für die indirekten potentiometrischen Bestimmungen von Kaliumpermanganat, Cer(IV)sulfat, Wasserstoffperoxyd, Kaliumpersulfat, -bromat und -dichromat vorgeschlagen. Der zu jeder der Substanzen in saurer Lösung zugegebene Überschuss an Eisen(II)äthylendiaminsulfat wird mit einer Vergleichslösung von Cer(IV)sulfat titriert. Man verwendet eine Platinfolie als Oxydation-Reduktions-Elektrode, welche mit einer gesättigten Kalomelelektrode mittels einer Agar-Agar-Kaliumchlorid-Brücke verbunden ist.

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OXIDATIONS WITH ALKALINE PERMANGANATE USING MONOVALENT THALLIUM FOR THE BACK TITRATION

IV. ESTIMATION OF HYDROGEN PEROXIDE

by

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Hydrogen peroxide is determined in two ways, directly and indirectly. The direct methods consist in the titration of hydrogen peroxide with potassium permanganate[1], with iodate[2] (after oxidation with hypoiodic acid) or with ceric solutions[3].

The indirect method[4] consists in treating hydrogen peroxide with an excess of hypobromite solution and titrating the excess hypobromite with arsenious oxide.

Hydrogen peroxide is known to reduce potassium permanganate in alkaline medium but the reaction was not studied quantitatively. The present investigation deals with this problem and a method is developed for the potentiometric determination of hydrogen peroxide with alkaline permanganate.

EXPERIMENTAL

Hydrogen peroxide solution was prepared by the appropriate dilution of AnalaR grade sample, with twice-distilled water. The concentration of the solution was determined by titration with potassium permanganate in presence of $\sim 1N$ H_2SO_4[1]. This solution was fairly stable and suffered only very slight decomposition ($\sim 4\%$) over a period of 3 days.

The other solutions, *viz.* monovalent thallium and permanganate, were prepared and standardized as previously described[5].

RESULTS

In studying this reaction we followed the same lines given in the previous investigations, *viz.* titration of potassium permanganate with hydrogen peroxide and oxidation of hydrogen peroxide with excess permanganate, followed by titration of the excess permanganate with monovalent thallium.

(1) *Titration of hydrogen peroxide with potassium permanganate*

In these titrations we were unable to obtain good results, owing apparently to the instability of hydrogen peroxide in alkaline medium. Decomposition of hydrogen peroxide was also catalysed by the precipitated manganese dioxide[6]. The end-points were always attained $\sim 70\%$ earlier than the theoretical ones. We then performed the reaction in presence of telluric acid which was thought to yield good results owing to its solvent action on manganese dioxide, but then the end-points were attained 45% earlier than the theoretical values. Trials to stabilize hydrogen peroxide by sodium pyrophosphate[7] or sodium silicate[8] did not lead to good results (*cf.* Table I).

TABLE I

TITRATION OF 5 ml H_2O_2 IN 0.1N NaOH WITH 0.1136N $KMnO_4$

Normality of H_2O_2	*Max. inflection per 0.1 ml $KMnO_4$ mV*	*Theoretical end-point ml*	*Experimental end-point ml*	*Error %*	*Other conditions*
0.0563	220	4.13	1.14	—72.4	
0.0563	205	4.13	1.24	—70.0	Sodium pyrophosphate
0.0563	135	4.13	2.15	—47.94	Telluric acid added
0.0563	205	4.13	2.27	—45.04	Telluric acid + sod. pyrophosphate
0.1074 (2.5 ml)	130	3.94	1.73	—56.09	Telluric acid + sod. silicate

In the absence of telluric acid, constant potentials were not readily attained; the potential rose slowly after the addition of $KMnO_4$ and separation of MnO_2, taking 2-4 minutes to become steady. Gas bubbles were always visible on the surface of the solid. However, in the presence of telluric acid the potentials rapidly acquired steady values after ∼1 min. In this latter case no manganese dioxide separated out but it is supposed that the catalytic effect of MnO_2 on the decomposition of H_2O_2 occurs on immediate addition of $KMnO_4$ before it becomes complexed with telluric acid. A titration curve representing the states of affairs is shown in Fig. 1.

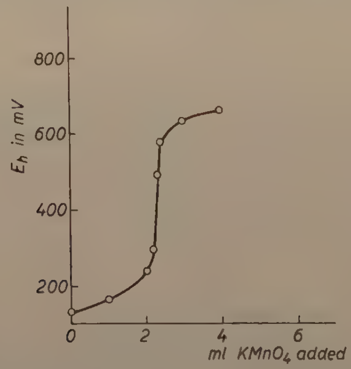

Fig. 1. Titration of 10 ml 0.0563N H_2O_2 in 0.1N NaOH with 0.1136N $KMnO_4$.

(2) *Titration of potassium permanganate with hydrogen peroxide*

Owing to the strong reducing action of hydrogen peroxide, reduction of permanganate passes rapidly to MnO_2. Even in the presence of Ba^{+2} ions (equivalent to four times the permanganate present) the end-points could not be checked at the manganate state. The end-points are nearly always attained later than the theoretical values, even when dilute hydrogen peroxide solutions are used (see Table II). It was then found impracticable to work in the presence of Ba^{+2} ions. The titration curves under these conditions possess only one single inflection which, although sharp, occurs later than the theoretical end-points.

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TABLE II

TITRATION OF $KMnO_4$ IN PRESENCE OF TELLURIC ACID WITH H_2O_2

Alkalinity	*Max. inflection per 0.1 ml H_2O_2 mV*	*Theoretical end-point ml*	*Experimental end-point ml*	*Error %*
Titration of 5 ml 0.1136N $KMnO_4$ with 0.08236N H_2O_2				
1N NaOH	201	4.13	4.14	+0.24
1N NaOH*	267	4.13	4.12	—0.24
3N NaOH	195	4.13	4.12	—0.24
Titration of 5 ml 0.1136N $KMnO_4$ with 0.0811N H_2O_2				
0.5N NaOH	138	4.20	4.22	+0.48
2N NaOH	116	4.20	4.22	+0.48
3N NaOH*	156	4.20	4.215	+0.36
Titration of 5 ml 0.02272N $KMnO_4$ with 0.00811N H_2O_2				
0.5N NaOH*	80	8.4	8.43	+0.36
0.5N NaOH	64	8.4	8.43	+0.36

* Sodium pyrophosphate added to the reaction mixture.

When the reaction is performed in absence of both Ba^{+2} ions and telluric acid, end-points later than the theoretical values are encountered. This is possibly brought about by the catalytic decomposition of a small portion of H_2O_2 by the precipitated manganese dioxide before it reacts with the higher oxidation states of manganese. However, in presence of telluric acid, in which case manganese dioxide did not separate out, end-points coinciding with the calculated ones are attained. The results are good for concentrations of H_2O_2 varying from 0.08236N to 0.00811N and for alkalinities ranging between 0.5-3N. The titration curves are smooth and characterized by two inflections. The first inflection corresponds to the manganate state and occurs much later than the theoretical value while the second corresponds to MnO_2 and occurs in the region of the theoretical end-point. The latter inflections are sharp, amounting to ∼200 mV in the case of 0.1N solutions.

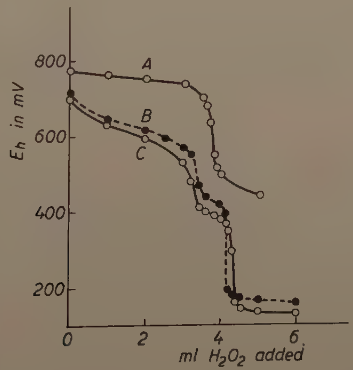

Fig. 2. (A) Titration of 10 ml 0.1136N $KMnO_4$ in 1N NaOH + Ba^{+2} ions with 0.08236N H_2O_2; (B) Titration of 5 ml 0.1136N $KMnO_4$ in 1N NaOH + telluric acid + sodium pyrophosphate with 0.08236N H_2O_2; (C) Titration of 5 ml 0.1136N $KMnO_4$ in 1N NaOH with 0.08236N H_2O_2.

The time necessary for equilibrium varies from stage to stage. At the beginning of the titration when the reaction involves reduction of $KMnO_4$, the equilibrium is rapid. Beyond the first inflection it takes $\sim$ 3 min in the presence and 5 min in the absence of telluric acid.

TABLE III

TITRATION OF $KMnO_4$ WITH H_2O_2 IN ABSENCE OF TELLURIC ACID

Alkalinity	*Max. inflection per 0.1 ml H_2O_2 mV*	*Theoretical end-point ml*	*Experimental end-point ml*	*Error %*
Titration of 5 ml 0.1136*N* $KMnO_4$ with 0.08236*N* H_2O_2 in absence of Ba^{+2} ions.				
1*N* NaOH*	105	4.13	4.32	+ 4.60
1*N* NaOH	184	4.13	4.34	+ 5.08
Titration of 5 ml 0.02272*N* $KMnO_4$ with 0.00811*N* H_2O_2 in absence of Ba^{+2} ions				
0.5*N* NaOH	61	8.4	8.63	+ 2.74
Titration of 10 ml 0.1136*N* $KMnO_4$ in presence of Ba^{+2} ions with H_2O_2				
1*N* NaOH**	82	2.81	3.74	+33.09
1*N* NaOH***	57	8.43	10.87	+28.94

* Sodium pyrophosphate added to the reaction mixture.
** Normality of H_2O_2 solution 0.0809.
*** ,, ,, ,, ,, 0.02697.

(3) *Oxidation of hydrogen peroxide by permanganate and back titrating excess oxidant with monovalent thallium*

From the foregoing study it becomes apparent that reduction of $KMnO_4$ in presence of Ba^{+2} ions does not give quantitative results on account of the fact that the reaction product is not one definite compound. The accuracy of the results in the presence of telluric acid makes it possible to develop an indirect method for the estimation of hydrogen peroxide consisting of the oxidation of H_2O_2 with excess $KMnO_4$ and titration of the excess oxidant with monovalent thallium. Since reduction of permanganate does not pass beyond the quadrivalent manganese stage in the presence of excess $KMnO_4$, it is not necessary to add H_2O_2 slowly as is the case when the reduction is to be checked at the manganate stage. It is sufficient to stir the solution in order to mix the reactants and, owing to the rapidity of the reaction, the excess oxidant can be immediately titrated with monovalent thallium. The method yields accurate results for small quantities of H_2O_2 down to 0.3 mg.

TABLE IV

DETERMINATION OF H_2O_2 USING Tl^+ FOR BACK TITRATION

Normality of Tl^+ = 0.0295

Vol. and Normality of $KMnO_4$	*Vol. and Normality of H_2O_2*	*H_2O_2 present mg*	*H_2O_2 found mg*	*Error %*
5 ml 0.1084*N*	3 ml 0.0941*N*	4.799	4.819	+0.42
5 ,, 0.1084*N*	2 ,, 0.0941*N*	3.199	3.185	—0.44
5 ,, 0.1084*N*	1 ,, 0.0941*N*	1.600	1.606	+0.38
10 ,, 0.02168*N*	3 ,, 0.01882*N*	0.960	0.960	nil
10 ,, 0.02168*N*	2 ,, 0.01882*N*	0.640	0.637	—0.47
10 ,, 0.02168*N*	1 ,, 0.01882*N*	0.320	0.318	—0.63

SUMMARY

Owing to the instability of hydrogen peroxide in alkaline solutions, direct oxidation with $KMnO_4$ did not yield accurate results. The back titration of $KMnO_4$ in the presence of 1*N* NaOH and Ba^{+2} ions also gave inaccurate results. The reaction could not be checked at the manganate state. However, in the presence of 2*N* NaOH and telluric acid quantitative data were obtained, which is not the case if telluric acid is absent.

Another advantageous method is the oxidation of hydrogen peroxide with excess $KMnO_4$ in the presence of 1*N* NaOH and telluric acid, followed by back titrating excess oxidant with monovalent thallium.

RÉSUMÉ

Vu l'instabilité du peroxyde d'hydrogène en solution alcaline, l'oxydation directe par $KMnO_4$ ne donne pas de résultats précis. Le titrage de l'excès de $KMnO_4$. en présence de NaOH *N* et d'ions Ba^{+2}, donne aussi des résultats peu précis, la réaction ne pouvant être contrôlée au stade manganate. Par contre, en présence de NaOH 2*N* et d'acide tellurique, des résultats quantitatifs sont obtenus, ce qui n'est pas le cas en l'absence d'acide tellurique. La méthode consistant à oxyder H_2O_2 par un excès de $KMnO_4$, en présence de NaOH *N* et d'acide tellurique, et à titrer l'excès d'oxydant au moyen du thallium (I) présente aussi des avantages.

ZUSAMMENFASSUNG

Da Wasserstoffperoxyd in alkalischer Lösung sehr unbeständig ist, gab die direkte Oxydation mit $KMnO_4$ keine genauen Resultate. Die Rücktitration von $KMnO_4$ in Gegenwart von *N* NaOH und Ba^{+2}-Ionen ergab ebenfalls ungenaue Resultate. Die Reaktion konnte nicht im Manganat-Stadium geprüft werden. Wenn jedoch 2*N* NaOH und Tellursäure zugegeben werden, erhält man quantitative Resultate, was nicht der Fall ist, wenn Tellursäure nicht zugegeben wird. Eine andere vorteilhafte Methode besteht darin, die Oxydation von Wasserstoffperoxyd mit $KMnO_4$ in Gegenwart von *N* NaOH und Tellursäure vorzunehmen, und dann den Überschuss des Oxydationsmittels mit einwertigem Thallium zurückzutitrieren.

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OXIDATIONS WITH ALKALINE PERMANGANATE USING MONOVALENT THALLIUM FOR THE BACK TITRATION

V. ESTIMATION OF HYDRAZINE

by

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The volumetric estimation of hydrazine is based on its tendency to become oxidized to nitrogen and water. Oxidizing agents usually used are iodate[1,2], bromate[2] or iodine[3].

Oxidation of hydrazine is a complex problem as it gives rise to various products in addition to nitrogen and water *e.g.* ammonia or hydrazoic acid. According to HIGGINSON, SUTTON AND WRIGHT[4], the consumption of oxidizing agent per mol of hydrazine will be lower if hydrazine is kept in excess than if the oxidizing agent is kept in excess. This suggests that direct titration of hydrazine by oxidizing agents gives rise to lower results whereas the reverse process of titration leads to accurate values. The direct oxidation of hydrazine by potassium permanganate in alkaline medium has not yet been applied as an analytical method and it is the aim of the present investigation to deal with this subject.

EXPERIMENTAL

Hydrazine solutions are prepared from hydrazine sulphate, by dissolving the AnalaR product in twice-distilled water. The concentration of hydrazine was determined by the iodate method, using chloroform as a solvent for the liberated iodine.

The permanganate solutions are prepared according to the method of STAMM[5] and standardized by the acid oxalate method[6]. The experimental technique and procedure is the same as described previously[7].

RESULTS

Oxidation of hydrazine with permanganate

Hydrazine is a strong reducing agent in alkaline medium if the process involves the formation of nitrogen and water. The E_0 value of the system N_2H_4/N_2 amounts to -1.16[8] volt at unit $[OH^-]$. This potential together with that of the MnO_4^-/MnO_2 couple[8] corresponds to an equilibrium constant and a degree of completion amounting to $3 \cdot 10^{-366}$ and $1.6 \cdot 10^{-51}$ respectively for the reaction between permanganate and hydrazine in alkaline solutions.

The results obtained on directly titrating hydrazine with $KMnO_4$ are shown in Table I and represented graphically in Fig. 1. The data indicate that the end-points are attained much earlier than the theoretical values owing to the tendency of hydrazine to become oxidized by atmospheric oxygen in alkaline solutions[9]. Atmos-

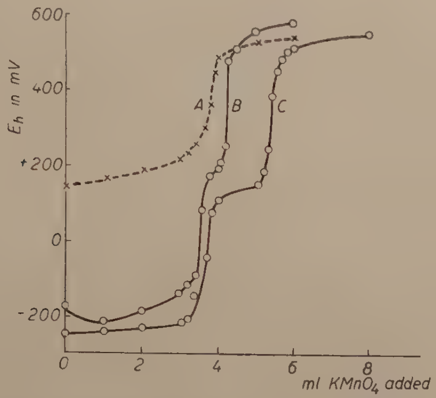

Fig. 1. (A) Titration of 10 ml 0.004548*N* N_2H_4 with 0.01084*N* $KMnO_4$ in the presence of telluric acid;
(B) Titration of 10 ml 0.04548*N* N_2H_4 with 0.1084*N* $KMnO_4$ in the absence of telluric acid;
(C) Titration of 10 ml 0.04548*N* N_2H_4 with 0.1084*N* $KMnO_4$ in the presence of telluric acid.

pheric oxidation is largely enhanced in presence of quadrivalent manganese as found experimentally. Thus it was observed that in unstirred solutions only 1% of hydrazine was decomposed after a period of one hour. On stirring 5% were decomposed after 15 min, the time taken to attain the first inflection, in the titration of hydrazine with permanganate. Oxidation of hydrazine was more enhanced in presence of the Mn^{+4}– tellurate complex prepared by mixing together equivalent amounts of hydrazine and $KMnO_4$ in the presence of telluric acid and 0.1*N* NaOH. Fig. 1 shows that in case of the more concentrated solutions titrated (0.04548*N*), the titration curves are characterized by two inflections. It is most probable that in the more concentrated solutions the reaction takes place in two steps, but the mechanism of the reaction is not clear in view of the decomposition of hydrazine.

TABLE I

TITRATION OF 10 ml 0.04548*N* HYDRAZINE WITH 0.1084*N* $KMnO_4$

Atmosphere	*Max. inflection* *1st step mV*	*2nd step mV*	*Theoretical end-point* $N_2H_4 \rightarrow N_2 + H_2O$ *ml*	*Exptl. end-point* *1st step ml*	*2nd step ml*	*Error 2nd step %*
Air	143	217	7.41	3.3	4.13	—44.26
,,	170	236	7.41	3.45	4.22	—43.05
,,	100	140	7.41	3.6	5.36	—27.67
Nitrogen	70	152	7.41	3.5	5.65	—23.75
,,	58	163	7.41	3.6	5.73	—22.67
Hydrogen	70	156	7.41	4.5	6.57	—6.57

It is noteworthy to state that during the first step a white precipitate is produced if telluric acid is present which then redissolves to give a clear orange red solution at the second end-point. A white precipitate is also formed when hydrazine is mixed with an alkaline solution containing telluric acid and quadrivalent manganese.

The white precipitate is not formed on titrating $0.004548N$ N_2H_4 solutions and the curve is characterized by a single inflection (curve A, Fig. 1). The end-points are attained much earlier than in the case of the more concentrated solutions owing to the increased instability of the more dilute hydrazine solution in presence of alkali.

Reduction of permanganate with hydrazine

In contradistinction from the foregoing reaction, titration of permanganate with hydrazine should give quantitative results. The presence of excess oxidant apparently favours the oxidation of hydrazine to nitrogen and water. According to HIGGINSON, SUTTON AND WRIGHT[4] the consumption of oxidizing agent per mole of hydrazine will be lower if hydrazine is kept in excess than if the oxidizing agent is kept in excess.

In these titrations reduction of permanganate takes place normally, *i.e.* in absence of Ba^{+2} ions MnO_2 is produced and the end-point coincides with the theoretical value irrespective of whether telluric acid is present or absent. In the presence of Ba^{+2} ions equivalent (or twice the equivalent) to permanganate, reduction of the latter is checked at the manganate state. Under these conditions and taking $E^\circ_{(HO)}MnO_4^-/MnO_4^{-2} = 0.564$ and $E^\circ_{(HO)}N_2H_4/N_2$ couple $= -1.16$ volt, the equilibrium constant and the degree of completion for the reaction $4\,Mn^{+7} + N_2H_4 + 4\,OH^- \rightarrow 4\,Mn^{+6} + N_2 + 4\,H_2O$ amount to $1.3 \cdot 10^{-117}$ and $4.2 \cdot 10^{-24}$ respectively.

TABLE IIA

TITRATION OF PERMANGANATE WITH HYDRAZINE IN THE ABSENCE OF Ba^{+2} IONS

Alkalinity	*Max. inflection 0.1 ml hydrazine soln. mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 5 ml $0.1084N$ $KMnO_4$ with $0.04548N$ hydrazine				
$0.5N$ NaOH*	214	7.15	7.17	+0.27
$1N$,,	138	7.15	7.14	—0.14
$2N$,, *	207	7.15	7.18	+0.41
$2.5N$,,	122	7.15	7.13	—0.27
Titration of 5 ml $0.0542N$ $KMnO_4$ with $0.01137N$ hydrazine				
$0.5N$ NaOH	22	14.3	14.27	—0.21
$1N$,,	21	14.3	14.25	—0.35
$1N$,, *	44	14.3	14.25	—0.35

* Telluric acid added to reaction mixture.

TABLE IIB

REDUCTION OF PERMANGANATE WITH HYDRAZINE IN THE PRESENCE OF Ba^{+2} IONS

Alkalinity	*Max. inflection 0.1 ml hydrazine soln. mV*	*Theoretical end-point ml*	*Exptl. end-point ml*	*Error %*
Titration of 5 ml $0.1084N$ $KMnO_4$ with $0.04548N$ hydrazine				
$1N$ NaOH	160	2.38	2.37	—0.42
$0.75N$,,	159	2.38	2.37	—0.42
Titration of 5 ml $0.0542N$ $KMnO_4$ with $0.01137N$ hydrazine				
$1N$ NaOH	137	4.76	4.74	—0.42
$0.75N$,,	126	4.76	4.77	+0.21

In the presence of Ba^{+2} ions the titration curve (curve A, Fig. 2) is characterized by a single inflection, whereas in its absence two inflections are observed (curve B, Fig. 2). The first of these corresponding to the manganate state is very poor and occurs later than the theoretical value, while the second corresponding to the manganese dioxide is very sharp and coincides with the theoretical value. In both cases the reaction is rapid.

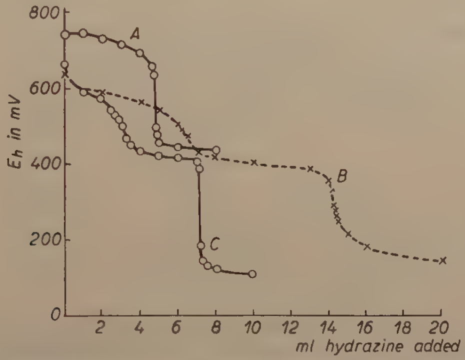

Fig. 2. (A) Titration of 5 ml 0.0542N $KMnO_4$ in 1N NaOH with 0.01137N N_2H_4 in the presence of Ba^{+2} ions;
(B) Titration of 5 ml 0.0542N $KMnO_4$ in 1N NaOH with 0.01137N N_2H_4 in the absence of Ba^{+2} ions;
(C) Titration of 5 ml 0.1084N $KMnO_4$ in 2N NaOH with 0.04548N N_2H_4 in the absence of Ba^{+2} ions.

Determination of hydrazine using monovalent thallium for back titration of excess permanganate

The above facts can be made use of in the determination of hydrazine by mixing with excess permanganate and back titrating excess oxidant with monovalent thallium. The process can be performed in the presence of Ba^{+2} ions, whereby reduction of $KMnO_4$ is checked at the manganate state. In this case the addition of hydrazine

TABLE III

DETERMINATION OF HYDRAZINE USING Tl^+ FOR BACK TITRATION OF PERMANGANATE

$Tl^+ = 0.0295N$, NaOH = 1N

Vol. and Normality of $KMnO_4$	*Vol. and Normality of hydrazine*	*Hydrazine added mg*	*Hydrazine found mg*	*Error %*
5 ml 0.1048N*	5 ml 0.04548N	1.822	1.819	—0.17
5 ,, 0.1048N*	3 ,, 0.04548N	1.093	1.098	+0.46
5 ,, 0.1048N**	2 ,, 0.04548N	0.730	0.732	+0.27
5 ,, 0.1048N**	1 ,, 0.04548N	0.364	0.365	+0.27
5 ,, 0.1048N*	1 ,, 0.04548N	0.364	0.362	—0.55
5 ,, 0.0524N*	5 ,, 0.01137N	0.455	0.453	—0.44
5 ,, 0.0524N*	2 ,, 0.01137N	0.182	0.183	+0.55
5 ,, 0.0524N**	2 ,, 0.01137N	0.182	0.181	—0.55

* Titration carried out in presence of telluric acid.
** Titration performed in presence of Ba^{+2} ions.

should be made slowly and with constant stirring to avoid reduction of $KMnO_4$ below the manganate state.

The estimation can also be made in the absence of Ba^{+2} ions when reduction of permanganate passes to quadrivalent manganese. This process should be performed in the presence of telluric acid since although quantitative reduction of $KMnO_4$ occurs in the absence of telluric acid by hydrazine, this is not the case with monovalent thallium. With this latter reagent telluric acid should be present to prevent the formation of lower oxides of manganese[10].

The results shown in Table III indicate that the process is applicable to small amounts of hydrazine as low as 0.182 mg.

SUMMARY

Oxidation of hydrazine in alkaline solutions with $KMnO_4$ gives inaccurate results both in the presence of absence of telluric acid. The titration curve is characterized by two inflections.

Titration of $KMnO_4$ with hydrazine gives good results in the presence of Ba^{+2} ions and 0.75-1N NaOH (when MnO_4^- gives MnO_4^{-2}) or in the presence of 0.5-2.5N NaOH only (when MnO_4^- gives MnO_2).

Hydrazine could be estimated by oxidation with $KMnO_4$ either in the presence of Ba^{+2} ions or telluric acid, after which the excess permanganate is back titrated with monovalent thallium. The alkalinity is kept at 1N NaOH.

RÉSUMÉ

L'oxydation de l'hydrazine, en solution alcaline, au moyen de $KMnO_4$ donne des résultats peu précis, en présence ou en l'absence d'acide tellurique. Les courbes de titrage sont caractérisées par deux inflexions. Le titrage de $KMnO_4$ par l'hydrazine donne de bons résultats, en présence de Ba^{+2} et de NaOH 0.75 à 1N (dans ce cas MnO_4^- se réduit en MnO_4^{-2}), ou en présence de NaOH 0.5 à 2.5N seulement (dans ce cas MnO_4^- se réduit en MnO_2). L'hydrazine peut être dosée par addition d'un excès de $KMnO_4$, en présence de NaOH N, on titre ensuite l'excès d'oxydant par le thallium(I).

ZUSAMMENFASSUNG

Die Oxydation von Hydrazin in alkalischer Lösung mit $KMnO_4$ gab ungenaue Ergebnisse sowohl in Gegenwart als auch in Abwesenheit von Tellursäure. Die Titrationskurve weist zwei Inflektionspunkte auf. Die Titration von $KMnO_4$ mit Hydrazin gibt gute Resultate; in Gegenwart von Ba^{+2} Ionen und 0.75-1N NaOH wird MnO_4^- zu MnO_4^{-2} reduziert; in Gegenwart von 0.5-2.5N NaOH allein, bildet sich MnO_2 aus MnO_4^-. Hydrazin kann bestimmt werden durch Oxydation mit $KMnO_4$ in Gegenwart von Ba^{+2}-Ionen oder von Tellursäure, und Rücktitration von überschüssigem Permanganat mit einwertigem Thallium. Die Alkalinität wird auf 1N NaOH gehalten.

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A POTENTIOMETRIC DETERMINATION OF POTASSIUM ETHYL XANTHATE

by

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INTRODUCTION

It is known, that xanthates in general, react with Cu^{+2} to give insoluble Cu-xanthate-compounds, according to

$$2\ C_2H_5\text{-O-CS.SK} + Cu^{+2} \rightarrow (C_2H_5\text{-O-CS.S})_2Cu\downarrow + 2\ K^+.$$

Xanthates may be formed by the reaction of carbon disulphide with an alkanol in alkaline medium. If both reactions are sufficiently rapid and quantitative and if it is possible to determine the end-point of the reaction of a xanthate with Cu^{+2} accurately, carbon disulphide may be determined quantitatively using both reactions. To answer these questions, it was investigated, whether xanthate can be titrated potentiometrically with Cu^{+2}. In this investigation use will be made of potassium ethyl xanthate, formed by the reaction of carbon disulphide and ethanolic KOH.

EXPERIMENTAL

A standard solution of potassium ethyl xanthate was prepared by weighing about 0.8 g of pure carbon disulphide to the nearest 0.1 mg in a sealed, thin-walled glass tube, and placing this tube in a solution of 0.1*N* ethanolic KOH, breaking the tube by shaking, and making up to 100 ml by addition of 0.1*N* ethanolic KOH. A 50-ml aliquot of this solution was diluted to 1 l with 0.1*N* ethanolic KOH. This solution thus contains about 0.4 mg of CS_2 per ml.

From preliminary experiments it could be shown, that when an aliquot of this standard solution is titrated potentiometrically with a solution of Cu(II)-acetate, which contains acetic acid, using a copper electrode as an indicator electrode and a saturated calomel electrode as a reference electrode, a sharp E.M.F.-drop occurs at the end-point of the reaction. To establish whether precise and accurate results could be obtained in this way, a number of determinations was carried out in the following way:

Aliquots of the standard solution were diluted with water to about 200 ml. This solution was titrated potentiometrically with 0.02*N* Cu(II)-acetate solution which contained 140 ml of 4*N* acetic acid per l. A copper electrode was used as an indicator electrode and a saturated calomel electrode as a reference electrode. The E.M.F. was measured with a Beckman pH-meter, model H 2.

24 Determinations were carried out on three different quantities of the standard solution. The average results are given in Table I. In this table CS_2 calc. is calculated assuming that CS_2 reacts quantitatively with ethanolic KOH to give potassium ethyl xanthate. The end-point of the titration is calculated with the aid of the second derivative of E.M.F. to ml of standard Cu-solution consumed. The precision is expressed in terms of the standard deviation in mg of CS_2. The combined standard deviation is 0.038 mg of CS_2 so that the precision is to be considered satisfactory. When the differences found are tested statistically using the *t*-test, it is found, that only for the smallest quantity of CS_2 accurate results are obtained. In both other cases the results are significantly low.

TABLE I

CS_2 calc.	*CS_2 found*	*Difference*	*Standard dev.*	*Number of detns.*
2.074 mg	2.076 mg	+0.002 mg	0.037 mg	8
4.149 ,,	4.112 ,,	—0.037 ,,	0.026 ,,	8
8.298 ,,	8.209 ,,	—0.089 ,,	0.046 ,,	8

Since the xanthate solution may become acid by additon of the acid Cu-solution and since it is known, that xanthates decompose in acid medium, the pH at the equivalence point was measured in all three cases.

Table II shows the values found.

TABLE II

CS_2 calc.	pH *at the end-point*
2.074 mg	9.0
4.149 ,,	4.3
8.298 ,,	4.2

The large discrepancy in pH values in Table II suggests that the low results are indeed due to decomposition of the xanthate. To establish the relation between pH of the xanthate solution at the equivalence point and the quantity of CS_2 found by titration, buffered solutions of potassium ethyl xanthate were titrated potentiometrically with a solution of 0.02*N* Cu(II)-acetate, which was as low as 0.02*N* in acetic acid to minimize the influence of the acid in the standard Cu-solution on the final pH. The results are given in Table III.

TABLE III

CS_2 calc.	*CS_2 found*	*CS_2 lost*	pH
6.425 mg	6.445 mg	—0.020 mg	5.8
	6.170 ,,	—0.255 ,,	5.5
	5.972 ,,	—0.453 ,,	5.0
	5.176 ,,	—1.249 ,,	4.5
	5.053 ,,	—1.372 ,,	4.0

From this table it is seen that the xanthate decomposes below pH 5.8. This means that during the titration the pH of the solution should not become lower than 5.8. On the other hand, the pH should not exceed 7.0 in order to prevent the precipitation of cupric hydroxide. It was found that in titration of solutions previously buffered between pH = 7.0 and pH = 5.8 the E.M.F.-drop at the equivalence point is rather small, thus reducing the precision of the end-point determination.

It is necessary therefore to titrate with a Cu(II)-acetate solution, which contains a very small amount of acetic acid and neutralize the xanthate solution with acetic acid prior to titration.

On these considerations a recommended procedure has been developed.

RECOMMENDED PROCEDURE

Neutralize the solution of potassium ethyl xanthate in ethanolic KOH, containing 1 to 10 mg of CS_2, with 0.1*N* acetic acid to pH = 7.0, using a pH-meter. With constant stirring titrate potentiometrically with 0.02*N* Cu(II)-acetate solution, which contains 6 ml of 1*N* acetic acid per l, using a copper electrode as an indicator electrode and a saturated calomel electrode as a reference electrode. If possible, apply a counter-voltage of 0.5 to 1.0 V, because the sign of the E.M.F. reverses during the titration. Calculate the end-point with the aid of the second derivative of the E.M.F. to ml of standard Cu-solution consumed.

Standardize the Cu(II)-acetate standard solution by electrolytic determination of the Cu-content of the Cu(II)-acetate in the preparation of the standard solution.

RESULTS

Following this procedure 12 determinations were carried out starting from three different quantities of potassium ethyl xanthate. The average results are given in Table IV.

TABLE IV

CS_2 *calc.*	CS_2 *found*	*Difference*	*Standard dev.*	*Number of detns.*
1.980 mg	1.974 mg	—0.006 mg	0.056 mg	4
3.961 ,,	3.943 ,,	—0.018 ,,	0.026 ,,	4
7.922 ,,	7.902 ,,	—0.020 ,,	0.038 ,,	4

The combined standard deviation is 0.042 mg of CS_2. From Table IV it is seen that the precision is very satisfactory again. When the standard deviations shown in Table I are compared with those shown in Table IV, it proves that the pH does not significantly influence the standard deviation. Therefore the standard deviations shown in Table I and Table IV are combined to obtain a better estimate of the true standard deviation. The combined standard deviation is 0.039 mg of CS_2.

The *t*-test applied to the average difference indicated that there is no reason to assume that the amount of carbon disulphide found deviates significantly from the amount present; with the null hypothesis that there is no difference the probability of our findings is 0.25. The E.M.F.-drop at the end-point in this case is about 86 mV; the titration curve is represented in Fig. 1.

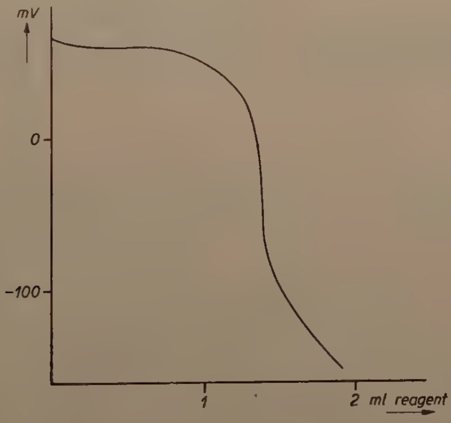

Fig. 1

CONCLUSIONS

From the results the following conclusions may be drawn:

1. The satisfactory agreement between the calculated values and the values found proves that the reaction between CS_2 and ethanolic KOH to form potassium ethyl xanthate is rapid and quantitative.
2. The reaction between potassium ethyl xanthate and Cu^{+2} is so rapid as to ensure a quick establishment of the E.M.F.
3. Potassium ethyl xanthate decomposes at a pH under 5.8.

4. There is no reason to assume that the carbon disulphide used in the preparation of the standard solution contains less than 100% CS_2.
5. In view of foregoing conclusions it may be said that CS_2 can be determined with good precision (standard deviation = 0.039 mg of CS_2).

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SUMMARY

A potentiometric determination of potassium ethyl xanthate with Cu(II)-acetate is described. From the results it follows that CS_2 reacts quantitatively with ethanolic KOH to give potassium ethyl xanthate. The method may therefore be used for the determination of CS_2.

RÉSUMÉ

Une méthode potentiométrique est décrite pour le dosage de l'éthylxanthogénate de potassium au moyen de l'acétate de cuivre. Les résultats prouvent que la formation de l'éthylxanthogénate de potassium, à partir du sulfure de carbone et de l'hydroxyde de potassium, en solution alcoolique est quantitative. La méthode proposée peut donc être utilisée pour le dosage du sulfure de carbone.

ZUSAMMENFASSUNG

Es wird die potentiometrische Bestimmung von Kalium-äthylxanthogenat mit Kupfer(II)acetat beschrieben. Die Resultate zeigen, dass CS_2 quantitativ mit äthanolischer Kalilauge reagiert, um Kaliumäthylxanthogenat zu bilden. Folglich kann die Methode für die Bestimmung von CS_2 verwendet werden.

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IODIMETRIC ESTIMATION OF ASCORBIC ACID WITH THE PLATINUM-TUNGSTEN BIMETALLIC ELECTRODE SYSTEM

by

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INTRODUCTION

Although a platinum electrode immersed in an oxidation-reduction solution indicates the reversible potential of the system, a tungsten electrode does not do so[1-4]. At equivalence therefore, whereas the potential of the Pt electrode varies suddenly, that of the W electrode remains unchanged. The Pt-W bimetallic electrode system, successful in inorganic oxidation-reduction electroanalysis, has recently been extended[5] in this laboratory to the estimation, by the bromination method, of readily and quantitatively brominated organic compounds, *e.g.* aromatic amines, phenols, *etc.* It appeared of interest therefore, to investigate the applicability of the system to the iodimetric estimation of ascorbic acid as recommended in the B.P.[6].

EXPERIMENTAL

The experimental arrangement and the electrical circuit are shown in Fig. 1. A Pyrex cell C fitted with Pt and W electrodes, a source of constant e.m.f. (1.5 volts) E, a variable resistance R (1.5 kΩ) and a sensitive galvanometer G were connected in series. The resistance R was adjusted initially, with C excluded, for full scale deflexion of the galvanometer. AnalaR grade ascorbic acid was further purified by repeated crystallization. A weighed amount (0.05-0.15 g) of the pure substance dissolved in water and acidified with sulphuric acid to a $2N$ solution was taken in C. Galvanometer deflexions were noted after successive additions, from a burette, of small amounts of a standard iodine solution and thorough mixing. Observations were continued, in each case, beyond the point of equivalence. Volumetric glass-ware used were of NPL class A standard. The temperature of the cell, the solutions and the measuring vessels was maintained at 25.0 ± 0.2° C in an air thermostat. A representative set of results is shown graphically in Fig. 2.

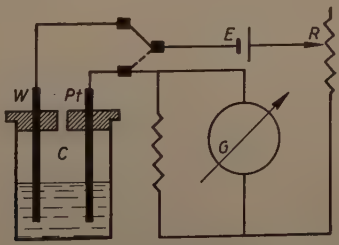

Fig. 1. The Pt-W bimetallic electrode system.

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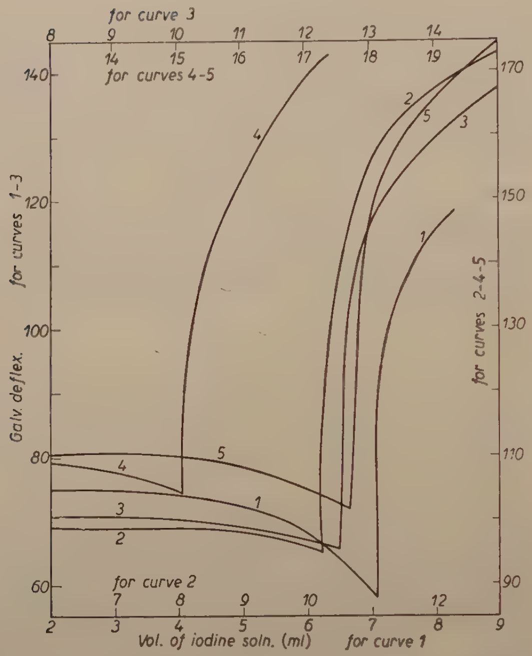

Fig. 2. Estimation of ascorbic acid with the Pt-W bimetallic system (curve 1, 0.0574 g; 2, 0.0828 g; 3, 0.1020 g; 4, 0.1218 g; 5, 0.1430 g).

DISCUSSION OF THE RESULTS

Each curve in Fig. 2 is characterized by a markedly defined break, the position of which corresponds quantitatively to the amount of iodine required by the reaction

$$C_6H_8O_6 + I_2 = C_6H_6O_6 + 2\ HI.$$

The weights of ascorbic acid taken and those calculated are contained in Table I.

TABLE I

	Wt. of ascorbic acid (g)	
Taken	*Found*	*Error*
0.0574	0.05718	—0.00022
0.0828	0.08271	—0.00009
0.1020	0.1013	—0.0007
0.1218	0.1219	+0.0001
0.1430	0.1431	+0.0001

An examination of data in Table I shows that the error is generally far less than that usually met with in ordinary volumetric estimations; this is indicative of the fact that the Pt-W bimetallic electrode system is applicable to the quantitative determination of ascorbic acid by the iodimetric method.

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ACKNOWLEDGEMENT

Grateful thanks of the authors are due to Prof. S. S. JOSHI for his kind interest in the work.

SUMMARY

The Pt-W bimetallic electrode system is applicable to the quantitative iodimetric estimation of ascorbic acid. Errors are far less than those usually met with in ordinary volumetric analysis.

RÉSUMÉ

L'électrode bimétallique platine-tungstène peut être utilisée pour le dosage iodométrique de l'acide ascorbique. Les erreurs faites sont beaucoup plus faibles que celles observées lors des analyses volumétriques ordinaires.

ZUSAMMENFASSUNG

Die bimetallische Platin-Wolfram-Elektrode kann für die jodometrische Bestimmung der Ascorbinsäure verwendet werden. Die Fehler sind viel kleiner, als diejenigen der gewöhnlichen volumetrischen Analysen.

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BOOK REVIEWS

Analyse Qualitative Minérale by PAUL-E. WENGER, DENYS MONNIER AND YVONNE RUSCONI, Georg et Cie S.A., Genève, 1955, xviii + 315 pp. Fr.s. 25.—

Although it is not actually stated, this work may be considered to be a revision and amplification of *Traité de Chimie Analytique Qualitative Minérale* by Wenger, Duckert and Rusconi (1946).

It is based on the classical method of group separations but has many novel features: full use is made of microchemical reactions and organic reagents. Since Prof. WENGER has long been a member of the I.U.P.A.C. New Analytical Reagents Commission it goes without saying that only the best and well authenticated reactions are recommended.

The first part of the book (59 pages) deals with fundamental principles of importance to analysis, such as electrolytic dissociation, modern theories of acids and bases, oxidation-reduction, solubility product, induced and masked reactions. There follow the principal reactions of the cations (arranged in the order of conventional group analysis) and of the anions (190 pages). In the final practical part (55 pages) very valuable and detailed instructions are given for the treatment of unknown substances submitted for analysis. It is usually this part which gives so much trouble to the student, particularly when dealing with insoluble and intractable substances. He will find here very real practical guidance, obviously based on the authors' wide experience.

There are, in addition, tables giving dissociation constants, solubilities of salts, redox potentials, etc. The book is well produced, with stiff cloth-covered boards.

The reviewer would conclude by echoing the words of Prof. G. CHARLOT in the Preface: "C'est donc en toute confiance que l'on peut souhaiter la bienvenue à cette nouvelle édition".

N. STRAFFORD (Manchester)

Introduction to paper electrophoresis and related methods, by MICHAEL LEDERER, Elsevier Publishing Company, Amsterdam, Houston London, New York, 1955 xii + 206 pp., 70 illus., 37s, 6d.

Paper electrophoresis was first employed as a method for the separation of proteins. It has later been shown that the technique can be successfully applied to widely different classes of substances. Dr. LEDERER emphasizes this fact and omits a comprehensive review of the literature in favour of clarity.

After a short historical part, some electrochemical laws necessary for an understanding of the principles, and an outline of the theory of apparatus and the general aspects of the techniques are described. In this connection continuous electrophoresis and electrophoresis combined with chromatography are also dealt with. The applications of paper electrophoresis are treated in eleven chapters. Some of these review a few publications only, and it can be questioned if they merit a whole chapter. One chapter deals with physicochemical measurements, *i.e.* mobility and isoelectric point determinations. In the last part of the book some related methods are described. First, an account is given of zone electrophoresis in columns and throughs using supports such as glass beads, starch and cellulose powder. Zone electrophoresis inside gels is described in detail in the following chapter. The two final chapters deal with measurement of diffusion rates inside porous media and electrokinetic ultrafiltration, respectively.

The development of electrophoresis in stabilizing media into a routine method in numerous laboratories and the rapid increase in the number of publications has made a systematic treatise like Dr. LEDERER's very welcome. A somewhat more critical treatment of the material would have been valuable, but the reviewer is aware of the fact that the meagre information often available from the publications makes such a treatment difficult.

The book is well written and the contents well organized, and it can be recommended as an introduction to the field of zone electrophoresis and as a reference book for the research worker interested in separation methods.

PER FLODIN (Uppsala)

Mises au point de chimie analytique pure et appliquée et d'analyse bromatologique, publiées sous la direction de J. A. GAUTIER, Troisième série, Masson et Cie., Paris 1955. Un volume broché de 192 pages avec 48 figures. Prix: Fr. 1900.—.

Il s'agit d'une collection de conférences intéressantes faites à la Faculté de Pharmacie de Paris pendant l'année 1954-1955. Elle débute par une étude de DIDIER BERTRAND sur les oligo-éléments des denrées alimentaires et leur rôle nutritionnel. Ensuite, HENRI GUÉRIN donne une sélection d'analyses et de micro-analyses des gaz en insistant sur les méthodes récentes: films de savon, conduction thermique, magnétisme, infrarouge, spectrographie de masses. La plupart des données et schémas sont extraits de l'excellent traité du même auteur (Masson et Cie., Editeurs). On passe alors à une intéressante mise au point d'EDGAR LEDERER sur les acquisitions récentes en chromatographie (125 références des deux dernières années) en portant l'attention sur les séparations de produits biologiques. Une conférence de FERNAND PELLERIN nous rappelle les grands principes des dosages acidimétriques dans les solvants non aqueux tandis que JEAN PIEN passe en revue les méthodes connues pour le dosage de la matière grasse du lait.

Cependant, l'originalité et l'utilité de cette brochure portent sur l'article final dû à RENÉ POTTIER, relatif à la *documentation en chimie analytique*. Je l'ai déjà consulté plusieurs fois y trouvant toujours le renseignement cherché. Il ne s'agit pas là d'une sèche énumération de livres relatifs à la chimie analytique mais de leur présentation raisonnée, travail considérable qui porte peut-être sur une vingtaine ou une trentaine d'années. L'utilité de cet article est incontestable et il faut remercier l'auteur d'avoir bien voulu le laisser extirper de ses fichiers. Je lui ferai un tout petit reproche, celui de n'avoir pas mis l'accent suffisant sur le travail considérable que des savants consciencieux comme WENGER, GILLIS et VAN NIEUWENBURG ont effectué pour réaliser le 2ème Rapport des réactifs nouveaux.

CLÉMENT DUVAL (Paris)

Spektrochemische Betriebsanalyse. Mit praktischen Ratschlägen für die Ausführung spektrochemischer Analysen im Betriebslaboratorium von DR. HEINRICH MORITZ. Ferdinand Enke Verlag, Stuttgart, 1956. Zweite verbesserte Auflage, XV und 240 Seiten mit 65 Abbildungen und 19 Zahlentafeln. Geheftet DM 52.—, Ganzleinen DM 55.—.

L'auteur nous présente un manuel pratique et fidèle d'analyse spectrale, particulièrement intéressant pour les débutants dans les laboratoires industriels.

Dans la première partie de ce traité bien conçu et remarquablement simple et clair, nous trouvons les chapitres classiques traitant des principes fondamentaux, des différentes sources d'émission, des spectrographes, des appareils pour le dépouillement des spectres, de l'émulsion photographique et des principes de la spectrométrie. Dans la seconde édition, qui vient de paraître, l'auteur a fait mention des progrès récents de la technique spectrochimique, mais un espace trop limité leur a été réservé. On regrette qu'à côté d'une description détaillée des sources classiques beaucoup utilisées en Allemagne il ne traite d'avantage les sources nouvelles et très importantes des A.R.L., de Hilger, d'Optica, etc. Les méthodes d'analyse directe, particulièrement intéressantes et supplantant peu à peu les méthodes photographiques dans toutes les industries importantes auraient mérité plus d'attention, et il nous semble qu'il existe d'autres appareils à lecture directe que ceux des Etats-Unis et de l'Italie.

Dans la deuxième partie — la plus importante — l'auteur traite successivement l'analyse qualitative, l'analyse générale et l'analyse quantitative, s'intéressant surtout aux méthodes applicables dans l'industrie. Le chapitre traitant l'analyse générale est nouveau et intéressant. Chaque chapitre traite séparément l'analyse des solutions et l'analyse des matières solides, distinguant entre métaux et alliages d'une part et matières minérales d'autre part. Toutes les manipulations sont décrites de façon claire et complète, avec plusieurs détails pratiques de grande importance, basés sur une expérience personelle de plusieurs années.

Dans la troisième partie l'auteur fait la comparaison entre l'analyse chimique et spectrochimique au point de vue durée de l'analyse et matière consommée, tandis que dans la quatrième partie il nous présente — à titre d'exemple — des conditions opératoires, essayées et appliquées avec succès à l'analyse de l'aluminium et de l'acier.

Malgré l'objection faite, le manuel peut être recommandé au spectrochimiste de tout laboratoire industriel qui y trouvera pour chaque cas particulier des renseignements utiles et très importants.

J. EEKHOUT (Gand)

Qualitative Schnellanalyse nach Charlot, von A. SCHLEICHER, 2. Auflage, Walter de Gruyter u. Co., Berlin, 1956, 90 Seiten. Geh.: DM. 7.80.

Das Buch enthält in der Hauptsache die Beschreibungen von Nachweisreaktionen für die häufigeren Kat- und Anionen. Der erste Teil ist eine Übersetzung des Buches *Analyse qualitative rapide des cations* von CHARLOT, BÉZIER u. GAUGUIN, der zweite gibt den Inhalt einer Arbeit von ODEKERKEN [*Z. anal. Chem.* 131 (1950) 165] über Nachweis von Anionen wieder. Nach den gegebenen Arbeitsvorschriften soll jedes der besprochenen Ionen neben größeren Mengen irgendeines anderen oder der Gesamtheit der anderen Ionen nachzuweisen sein. Trennungen werden nach Möglichkeit vermieden. Bei den meisten Einzelreaktionen wird auf einige Störungsmöglichkeiten hingewiesen, doch können diese, dem Umfang des Bändchens entsprechend, nicht vollständig erfaßt sein. Falls sich der Benutzer dieser Tatsache bewußt ist und ihn die Erkennung kleiner Gehalte nicht interessiert, mag der Inhalt des Buches hier und da nützlich sein.

Der analytisch arbeitende Chemiker hat schon lange, wenn nur der Nachweis einzelner Bestandteile einer Probe zur Rede stand, Trennungen und Nachweisreaktionen, die für den speziellen Fall besonders geeignet erschienen, angewandt und nicht irgendeinen Trennungsgang durchgearbeitet. Insofern kann man hier wohl kaum von einem neuen Wege sprechen, wie das der Herausgeber tut. Faßt man allerdings diesen ,,neuen Weg'' so auf, daß man eine qualitative Analyse nun nur noch auf dem Wege einer Aneinanderreihung derartiger Einzelnachweise durchzuführen gedenkt, so ist das eine nicht zu vertretende Simplifizierung der beim praktischen analytischen Arbeiten vorliegenden Verhältnisse, die entweder auf Kosten der Nachweisempfindlichkeit oder der Eindeutigkeit des Nachweises gehen muß.

Gegenüber den grundsätzlichen Bedenken gegen die in dem Buche vertretene Tendenz sind alle nnderen Bemerkungen, die zu machen wären, von zweitrangiger Bedeutung. Die mit einer gewissen Einseitigkeit ausgewählten Nachweisreaktionen sind von unterschiedlicher Empfindlichkeit und Leistungsfähigkeit. Kleinere Unkorrektheiten finden sich an mehreren Stellen.

H. BODE (Hannover)

Technisch — chemische Analyse, von L. MEDICUS UND H. REUTHER, 6. Auflage, Theodor Steinkopff, Dresden und Leipzig, 1955, 231 Seiten, 57 Abb. DM. 9.—.

In dem vorliegenden Buche werden in kurzer, übersichtlicher Weise die wesentlichen Verfahren der technisch-chemischen Analyse besprochen. Im I. Teil werden zunächst die bei der Probenahme zu beachtenden allgemeinen Gesichtspunkte dargestellt und dann die wichtigsten technisch verwendeten Methoden der Untersuchung des Wassers, fester und flüssiger Brennstoffe, der Schmiermittel sowie die technische Gasanalyse in den Grundzügen beschrieben. Der II. Teil bringt eine Beschreibung kolorimetrischer und photometrischer Methoden, gewichtsanalytischer Schnellverfahren und gasvolumetrischer Methoden. Nach kurzer Besprechnung der Begriffe und einfacher Apparaturen werden Beispiele für die Anwendung dieser Verfahren gegeben, die so ausgewählt sind, daß sie besonderes technisches Interesse besitzen. Der III. Teil behandelt die Untersuchung der Erze (Hüttenprodukte) und Metalle sowie der Düngemittel an einigen ausgewählten Beispielen. Im Anhang sind Angaben über technische Temperaturmessungen und Messungen des pH-Wertes gemacht.

Entsprechend der Aufgabe, die sich der Bearbeiter gestellt hat, liegt das Hauptgewicht bei der Beschreibung solcher Verfahren, die mit verhältnismäßig geringen Mitteln als Routinebestimmungen im Betriebslaboratorium durchgeführt werden können, theoretische Betrachtungen sind demgemäß auf das Mindestmaß beschränkt, das zu einem anschaulichen Verständnis der Dinge ausreicht. Eine größere Anzahl von Literaturhinweisen, die sich allerdings überwiegend auf ältere Arbeiten beziehen, wird von manchem Benutzer als nützlich empfunden werden. Bei der Auswahl der einzelnen Arbeitsverfahren wurden weitgehend DIN-Vorschriften berücksichtigt.

Das Buch kann als eine für manches kleinere Betriebslaboratorium geeignete und ausreichende Sammlung von Arbeitsvorschriften empfohlen werden, daneben ist es sicherlich auch als Hilfsbuch bei der Ausbildung von Chemielaboranten und Chemotechnikern gut geeignet.

H. BODE (Hannover)

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SUBJECT INDEX

Chr. = Chromatography — chromatographie — chromatographische Analyse
Col. = Colorimetric, heterometric, photometric and spectrophotometric analysis — colorimétrie, hétérométrie, photométrie et spectrophotométrie — heterometrische, kolorimetrische, photometrische und spektrophotometrische Analyse
El. = Electrical methods (except polarography) – Méthodes électriques (excepté polarographie) — Elektrische Methoden (ausgenommen Polarographie)
Grav. = Gravimetric and thermogravimetric (*) analysis — gravimétrie et thermogravimétrie (*) — gravimetrische und thermogravimetrische (*) Analyse
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M. = Miscellaneous — divers — Verschiedenes
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